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127PE3

JOURNAL

OF

THE CHEMICAL SOCIETY

CONTAINING

PAPERS COMMUNICATED TO THE SOCIETY

1925, VOL. 127, OCTOBER

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CCXCIII.—*The Velocity of Benzylation of certain Amines. Part II.*

By David Henry Peacock.

In a previous paper (J., 1924, **125**, 1975), the energies of activation for the reaction between benzyl chloride and aniline or *p*-toluidine, and between *p*-nitrobenzyl chloride and aniline or *p*-toluidine were calculated from the velocity coefficients at two temperatures; no evidence was found that these energies are additive in character. The results of some further experiments are now described, but before their bearing on the nature of the process of activation is discussed the effect of substitution and other factors will be dealt with.

m-Nitrobenzyl chloride always reacted faster than *p*-nitrobenzyl choride with the bases used. Olivier (*Rec. trav. chim.*, 1922, **41**, 646) obtained similar results in their hydrolysis. Slator and Twiss (J., 1909, **95**, 99) found that the order was reversed with sodium thiosulphate, where reaction is taking place with the negative thiosulphate ion. These results can be explained on the alternate polarity hypothesis. With bases such as aniline and dimethylaniline nitrobenzyl chlorides react more slowly than does benzyl chloride, although it might be expected that the general polar effect of the nitro-group would make the chlorine more reactive in nitrobenzyl than in benzyl chloride. These results may be explained by assuming that before reaction occurs the base and the halogen compound combine loosely and the negative substituent in the benzyl chloride then weakens the tendency of the nitrogen to form part of a positive ion and so reduces the rate of reaction. The results of other experiments described below show that the introduction of a nitro-group into the nucleus of the base considerably reduces the reaction velocity.

Additional evidence in support of this assumption can be obtained from the results of Jones and Preston (J., 1912, **101**, 1931) and of Thomas (J., 1913, **103**, 595), who obtained the following velocity coefficients in alcohol at 40° with dimethylaniline: benzyl bromide 6·34, *m*-xylyl bromide 8·62, *p*-xylyl bromide 23·2, *p*-bromobenzyl bromide 6·03. The positively substituted benzyl bromide reacts faster, and the negatively substituted benzyl bromide more slowly, than the unsubstituted bromide.

The effect of substitution in the nucleus of the base upon the velocity coefficient can be seen from the data given later. *m*-Nitroaniline reacts faster than *p*-nitroaniline, and *p*-toluidine faster than *m*-toluidine; results in accordance with the alternate polarity hypothesis.

The effect of concentration on the velocity coefficients and energies

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of activation is sometimes considerable and, as will be seen from the tabulated results, depends on the character of the base employed. Attention is also directed to the difference in the effect of alteration in concentration upon the velocity and energy of activation of the reaction between benzyl chloride and dimethylaniline.

Velocity coefficient and concentration.

Base.	Conc.	Conc. of benzyl chloride.	$k_{35°} \times 10^3$.	$k_{45°} \times 10^3$.	E, calories.
Aniline	0·4	0·2	3·62	8·5	16550
	0·8	,,	3·68	9·2	17770
	1·6	,,	4·07	10·55	18460
	1·6	0·4	4·25	11·2	18780
o-Toluidine	0·8	0·2		5·96	
	1·6	,,		7·1	
p-Toluidine	0·8	,,	5·96	14·7	17440
	1·6	,,	6·21	15·1	17230
p-Chloroaniline	0·4	,,		5·15	
	0·8	,,		5·08	
Monoethylaniline.....	0·8	,,		1·138	
	1·6	,,		1·13	
Dimethylaniline	0·8	,,	2·78	6·09	15210
	1·6	,,	2·23	5·06	15890
Diethylaniline	0·8	,,		0·400	
	1·6	,,		0·303	

Examination of the results obtained showed also an interesting connexion between energy of activation and the constitution of the substituted benzyl chloride used. When the energies of activation of *m*- and *p*-nitrobenzyl chlorides with aniline, *p*-toluidine, *o*-toluidine, and dimethylaniline are compared, it is seen that, although there is apparently no strictly quantitative additive relation, there is a qualitative relationship, the energy of activation for *m*-nitrobenzyl chloride being less than that for *p*-nitrobenzyl chloride. The alternate polarity theory would lead us to expect that the chlorine in *m*-nitrobenzyl chloride should be more reactive than that in *p*-nitrobenzyl chloride. This conclusion is seen to be confirmed, not only by the velocity data, but also by the activation energy data. Applying the Bohr theory of atomic structure, it may be said that the displacement of electrons postulated by the alternate polarity theory decreases the amount of energy required to take an electron in the chlorine atom to its activated position.

Energies of Activation in Methyl Alcohol.

Base.	Benzyl chloride.	*m*-Nitrobenzyl chloride.	*p*-Nitrobenzyl chloride
Aniline	17770	17280	18030
p-Toluidine.....	17440	14480	17100
o-Toluidine	15420	14210	17680
Dimethylaniline.....	15210	13120	15960

The results described below also throw some light on the process of activation. The influence of a nitro-group in the benzyl chloride on the velocity of reaction is similar to the influence of a nitro-group in the nucleus of the amine. Also there is no evidence that, in general, the energy of activation is an additive property (Arrhenius, *Z. physikal. Chem.*, 1889, **4**, 226). It is now suggested that the formation of a loose molecular complex precedes activation and the energy of activation measured in the cases cited is the energy of activation of such a complex.

Experimental.

The method of estimation was that already described (*loc. cit.*). The constants were calculated by the modified equation, taking into account the base combined with the liberated hydrochloric acid; Moore, Somervell, and Derry (J., 1912, **101**, 2459) have already directed attention to this omission in Menschutkin's calculations and their work should have been mentioned in the previous paper.

Tertiary bases gave much more constant values of the velocity coefficient than primary; difficulty was also experienced in getting concordant results with *p*-nitrobenzyl chloride. The bases used were crystallised as their hydrochlorides or acetyl compounds in the case of primary and secondary bases. The tertiary bases were tested for freedom from primary or secondary bases by the usual acetic anhydride test. The results are tabulated below.

Velocity coefficients in methyl alcohol.

Conc. of base, 0·8*M*. Conc. of chloride, 0·2*M*.

	Temp. 45°.			Temp. 35°.		
Base.	Benzyl chloride.	*m*-Nitrobenzyl chloride.	*p*-Nitrobenzyl chloride.	Benzyl chloride.	*m*-Nitrobenzyl chloride.	*p*-Nitrobenzyl chloride.
Aniline	0·0092	0·00451	0·00365	0·00368	0·00185	0·00144
p-Toluidine.....	0·0147	0·00874	0·00667	0·00596	0·00407	0·00276
o-Toluidine ...	0·00596	0·00256	0·00207	0·00269	0·00123	0·000832
Dimethylaniline	0·00609	0·00132	0·00092	0·00278	0·000671	0·000404

Velocity coefficients at 35° and at 45°.

(*See also a preceding table*).

Conc. of benzyl chloride, 0·2*M*.

m-Toluidine : conc. 0·8*M*; $k_{35°}$ 0·00494.
m-Nitroaniline : conc. 0·8*M*; $k_{45°}$ 0·00168.
p-Nitroaniline : conc. 0·4*M*; $k_{45°} > 0·0002$.
Monomethylaniline : conc. 0·8*M*; $k_{35°}$ 0·00644; $k_{45°}$ 0·0187.
Monobenzylaniline : conc. 0·8*M*; $k_{45°}$ 0·00335.
p-Bromodimethylaniline : conc. 0·8*M*; $k_{45°}$ 0·00175.

In conclusion, I wish to thank the British Dyestuffs Corporation, Huddersfield, who supplied many of the bases used in this work, and Mr. B. K. Menon, who prepared some of the *p*-nitrobenzyl chloride.

UNIVERSITY COLLEGE, UNIVERSITY OF RANGOON,
BURMA. [*Received, April 27th* 1925.]

CCXCIV.—*A New Peroxide of Barium.*

By MARGARET CARLTON.

WHEN hydrogen peroxide is added to a well-cooled, aqueous solution of barium hydroxide, white, crystalline $BaO_2,8H_2O$ is formed. If, however, excess of hydrogen peroxide be added, the appearance of the crystals changes and a granular precipitate is formed which rapidly settles after shaking. This becomes buff-coloured on standing. If this substance be filtered off and dried in a vacuum desiccator over phosphorus pentoxide, the colour slowly darkens for a day or two, until a deep buff colour is reached; on further standing, the colour fades and a creamy powder remains. This seems to suggest the formation and decomposition of an oxide higher than BaO_2.

A study of the action of excess of hydrogen peroxide on baryta was made by Schöne (*Annalen*, 1878, **192**, 257), and he showed the existence of a white, crystalline compound, BaH_2O_4, which turned yellow on standing. He suggested that this yellow compound might be BaO_3 or BaO_4, but he did not investigate the matter further. Traube and Schulze (*Ber.*, 1921, **54**, 1626) obtained a substance which on analysis seemed to be BaO_2 with not more than 5% BaO_4.

On the suggestion of Professor Baker, I have undertaken an examination of the action of hydrogen peroxide on barium hydroxide.

A preliminary analysis of the wet substance obtained by precipitation with hydrogen peroxide was therefore carried out, by means of potassium permanganate and dilute sulphuric acid, to determine the oxygen and barium, and this indicated the presence of a substance which seemed to be almost entirely BaO_3 or BaO_4.

Fresh samples of the substance were prepared in the following way: Pure crystalline barium hydroxide (10 g.) was dissolved in 200 c.c. of water, and 10 c.c. of 30% hydrogen peroxide were slowly added with repeated shaking, the temperature of the solutions being about 15°. For the first two preparations the mixture was

kept over-night at the ordinary temperature; the following morning, the precipitate was faintly buff-coloured and was washed by decantation with cold water and finally filtered through an alundum crucible, washed again with cold water, and finally with alcohol and ether, and dried in a vacuum over phosphorus pentoxide. Later on, the substance was kept only for 10—20 minutes after the addition of the hydrogen peroxide, for the precipitate to settle; it was then washed by decantation, filtered off, and washed with water only and dried in a vacuum over phosphorus pentoxide.

Properties.—The substance is a cream-coloured, non-crystalline powder, which darkens on standing.

When it is heated gently in a dried tube, moisture collects on the walls; this does not liberate iodine from potassium iodide and therefore is not hydrogen peroxide.

On extracting with ether and testing the extract for hydrogen peroxide, no trace was found, showing the absence of free hydrogen peroxide and also of hydrogen peroxide of crystallisation.

The solid substance decolorises neutral potassium permanganate more rapidly than barium dioxide, giving a brown colour and evolution of oxygen.

It does not liberate iodine from neutral potassium iodide even on standing, but when a few drops of dilute nitric acid are added, iodine is rapidly liberated; more iodine separates than from a similar amount of barium dioxide.

With neutral potassium bromide there is no action but on acidifying with a few drops of either nitric or hydrofluoric acid, bromine is freely liberated, whereas only a trace of bromine is produced from barium dioxide.

With strong hydrochloric acid, there is a vigorous action and chlorine is liberated freely; with barium dioxide only a trace of chlorine is produced.

When it is heated with flowers of sulphur a very vigorous action takes place; a peculiar odour is observed afterwards but no sulphur dioxide (compare barium dioxide, where there is a fairly vigorous action with formation of sulphur dioxide).

The foregoing tests show the presence of a very vigorous oxidising agent, and attempts to determine the amount of oxygen in the compound were made. Analyses had to be carried out before the substance was completely dry, owing to its instability. The oxide was only dried for about an hour over phosphorus pentoxide, in a vacuum; the first sample was then taken for analysis. Two analyses were made at the same time, by different methods. The first analysis consisted in determining the oxygen and water given off when the substance was heated in an atmosphere of

nitrogen. The apparatus used is shown in the accompanying sketch.

A weighed amount of the substance (1—2 g.) was introduced into a weighed Jena glass bulb, B. This was connected through a ground joint to a U-tube, C, containing calcium chloride and to the two tubes, D and E, containing freshly-reduced copper gauze. The tubes C, D, and E were weighed before and after each experiment.

Nitrogen, from which traces of oxygen were removed by passage over the heated tube, A, of copper, was slowly passed through the apparatus and when all the air had been displaced, the tubes, D and E, containing the copper gauze, were heated by means of electric furnaces to 500—600°. When these were hot, the bulb B was heated in a water-bath until the whole of the water in the oxide appeared to have been removed. This sometimes took as long as 3 hours; the bath was then removed and the bulb gently heated nearly to dull redness for a few minutes. The bulb was then allowed to cool; when it was cold, the furnaces heating D

FIG. 1.

and E were switched off and the whole apparatus was left to cool with the nitrogen bubbling through. When cold, the nitrogen was displaced by a slow current of dry air and the tubes C, D, and E and the bulb B were weighed.

The formula was calculated on the assumption that the residue was barium dioxide. This was found not always to be the case; barium dioxide decomposes somewhat when heated in a vacuum to 450° and, since the partial pressure of oxygen is here very small, possibly the same effect is produced and the proportion of oxygen calculated in this way may be rather high.

The weight of water collected in C was subtracted from the actual weight of oxide taken, to give the amount of anhydrous salt used in each experiment. The values of x in BaO_x are given in the table.

The second analysis of the substance was performed while the analysis described above was being carried out. A second sample of the oxide was examined for available oxygen and for barium.

A weighed amount of the salt, dissolved in dilute nitric acid, was titrated with potassium permanganate; the barium was then precipitated from the same solution and weighed as barium sulphate.

This gave an independent estimate of the barium and oxygen present.

The equation used in calculating the composition of the substance is :—

$$BaO_x + \tfrac{2}{5}(x-1)KMnO_4 + \{\tfrac{3}{5}(x-1)+1\}H_2SO_4 = BaSO_4 + \frac{x-1}{5}K_2SO_4 + \tfrac{2}{5}(x-1)MnSO_4 + \{\tfrac{3}{5}(x-1)+1\}H_2O + (x-1)O_2.$$

From which we get that 137 g. of barium correspond to $\frac{2}{5}(x-1)16$ g. of oxygen. And so the value of x can be calculated.

The results are given in the table.

Owing to the uncertainty as to the decomposition of the barium dioxide, a second method was used in liberating oxygen from the compound. Instead of heating the BaO_x in an atmosphere of nitrogen, the air was displaced from the apparatus as before and the weighed tubes containing the copper were heated, then a slow current of carbon dioxide was passed and the oxide heated as before; the residue was obtained as barium carbonate, which is quite stable at the temperature used.

Interval between preparation and analysis.	Value of x from dry analysis.	Value of x from wet analysis.	Interval between preparation and analysis.	Value of x from dry analysis.	Value of x from wet analysis.
About 4 hours	—	2·91	2 days	2·85	2·87
2 days	3·7	2·86	4 days	2·56	—
6 days	—	2·4		3·07	3·3*
immediately	—	2·91	Washed with water only.		
1 day	2·42	2·89	same day	2·99	—
1 day	3·04	2·99	1 day	2·68	2·87
3 days	2·73	2·55	same day	3·26	2·98
same day	3·91	2·9	same day	3·7	2·96
1 day	3·4	2·79	2 days	3·14	2·74
1 day	2·9	2·79		3·37	2·9
1 day	2·99	2·90	Residue obtained as barium carbonate.		
2 days	3·2	—	same day	2·89	2·71
3 days	2·8	2·63	1 day	2·83	—
			same day	2·77	—
			same day	2·96	3·21

Results bracketed together are different analyses of the same preparation.

* The preparation and determination of this sample were kindly carried out by Mrs. Muriel Baker.

Conclusion.

(1) By the action of an excess of hydrogen peroxide on barium hydroxide at temperatures below 20° a new substance is formed.

(2) This substance is unstable and is a vigorous oxidising agent, being much more reactive than barium dioxide, *e.g.*, liberates bromine from potassium bromide and chlorine very freely from hydrogen chloride.

(3) The results of analysis indicate that it probably has the formula BaO_3.

It is proposed to use this substance in an attempt to prepare a new peroxide of hydrogen. The work will be done in conjunction with Professor Baker and Mrs. Baker, repeating and extending experiments which they have already made with potassium tetroxide.

I wish to express my thanks to Professor Baker for his kind help and encouragement in this research.

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LONDON, S.W. 7. [*Received, July 4th*, 1925.]

CCXCV.—*The Action of Aldehydes on the Grignard Reagent. Part III.*

By JOSEPH MARSHALL.

ONLY when an aldehyde in less than one molecular proportion is allowed to react with an ethereal solution of a magnesium alkyl halide is the expected secondary carbinol the chief product of the reaction; if an excess is added, almost the whole of the excess is combined in some manner with the magnesium complex and the product obtained on decomposition of the mass with water is a mixture containing as one of its constituents the primary alcohol corresponding to the aldehyde used in the reaction (J., 1914, **105**, 527; 1915, **107**, 509). Papers recently published (Meisenheimer, *Annalen*, 1925, **442**, 180; Hess, *Annalen*, 1924, **437**, 256; Rheinboldt, *J. pr. Chem.*, 1925, **109**, 175) agree with the results of the author up to this point, but they differ both as to the mechanism by which the alcohol is supposed to be formed in the reaction and also as to the nature of the other products. Meisenheimer and Hess, whilst not in accord in detail, both suggest that the original co-ordination compound of magnesium ethyl bromide and benzaldehyde is capable of resolution in two directions indicated by the schemes :—

$$\text{(1) } PhCHEt{\cdot}OMgBr \leftarrow PhCHO + MgEtBr \rightarrow PhCH_2{\cdot}OMgBr + C_2H_4 \text{ (2)}$$

the second of these resolutions taking place to a much smaller extent than the first.

The reduction of the aldehyde is represented by this theory as being due to the addition of a hydrogen atom from the alkyl halide, and hence the alkylene evolved should be equivalent to the alcohol

produced. Meisenheimer points out that he has never observed this equivalence, but suggests that some isomerisation takes place.

When an aryl halide is used in the reaction, the author has shown that a primary alcohol is again formed. The scheme representing this would appear to be

$$PhCHO + MgPhBr \longrightarrow PhCH_2{\cdot}OMgBr + C_6H_4< \quad . \quad (3)$$

and this might reasonably be expected to result in the production of diphenylene, which, however, has never been observed in this reaction.

This theory does not explain the production of substances in the Grignard reaction under discussion other than the secondary alcohol, which is the normal product, and the primary alcohol corresponding to the aldehyde used in the reaction; the presence of any other compounds in the product of the reaction would entail a considerable extension of the theory.

The author (*loc. cit.*) showed that along with the primary and secondary alcohols obtained in a Grignard reaction the ketone corresponding to the secondary alcohol is formed, with condensation products of this ketone and the aldehyde used in the reaction. Thus, when benzaldehyde in excess reacts with magnesium methyl iodide, the products which may be isolated are benzyl alcohol, acetophenone, phenyl styryl ketone, and dibenzoylmethane, while the phenylmethylcarbinol which, normally, would be the main product of the reaction is almost entirely absent. Again, when benzaldehyde in excess reacts with magnesium phenyl bromide, the only products are benzyl alcohol and benzophenone, whilst with magnesium benzyl bromide, benzaldehyde produces, besides benzyl alcohol and deoxybenzoin, a large amount of phenyldibenzoylmethane.

The suggestion was hazarded in one of the earlier papers that the new reaction was analogous to Cannizzaro's reaction, in which one molecule of benzaldehyde oxidises a second molecule of the same aldehyde to benzoic acid, being itself reduced to benzyl alcohol. If this suggestion be correct, it is evident that when cinnamaldehyde is allowed to react with magnesium ethyl iodide as described by Meisenheimer, there is the possibility of the formation of styryl ethyl ketone and other condensation products along with cinnamyl alcohol and styrylethylcarbinol.

Since styryl methyl ketone is more easily identified than the ethyl compound, the experiment was first carried out with magnesium methyl iodide, with the result that whilst styryl methyl ketone was isolated as the phenylhydrazone in good yield, the only alcohol which could be obtained was cinnamyl alcohol. This was isolated

as the *p*-nitrobenzoyl ester (m. p. 76°; compare Meisenheimer, *loc. cit.*) and there was no indication of the presence of styrylmethylcarbinol either as its ester or as phenylbutadiene, which might have been formed as phenylpentadiene is produced when *p*-nitrobenzoyl chloride acts on styrylethylcarbinol. The corresponding reaction with magnesium ethyl iodide was performed with results similar to those obtained with magnesium methyl iodide, but in this case, by longer boiling of the reaction product, an attempt was made to secure the formation of more complicated products.

Since it has been shown in earlier papers that alkyl aldehydes are capable of reacting in a manner analogous to that in which aromatic aldehydes react, it was of interest to determine whether the simplest aldehyde, formaldehyde, would react similarly. The normal product of this reaction is the primary alcohol (*Compt. rend.*, 1902, **134**, 107), and it would be expected that excess of formaldehyde would oxidise part at any rate of the primary alcohol to the aldehyde. Accordingly, the reaction between magnesium phenyl bromide and trioxymethylene was investigated, with the result that a considerable quantity of benzaldehyde was isolated, although the chief product of the reaction was benzyl bromide (compare J., 1914, **105**, 534).

EXPERIMENTAL.

Action of Cinnamaldehyde on Magnesium Methyl Iodide.—An ethereal solution of cinnamaldehyde (132 g.; 1 mol.) was added to the Grignard solution prepared from magnesium powder (24 g.; 1 mol.) and methyl iodide (142 g.; 1 mol.), cooled in a freezing mixture. At first a yellow precipitate formed which immediately dissolved on shaking, but when about half the aldehyde had been added a greyish-white solid began to separate. Three hours later, a second molecule of cinnamaldehyde in ether was added quickly, whereby the precipitate was changed into a viscous, yellowish-brown material. After 12 hours, the mixture was heated on the steam-bath during 10 hours and cooled, and the ether was poured into ice and hydrochloric acid, separated, and shaken with sodium bisulphite solution, when about 2 g. of the bisulphite compound of cinnamaldehyde separated. From the residual ether 2 g. of a dark-coloured, sticky material was obtained which was not examined.

The heavy, yellow mass from which the ether had been poured was shaken with ice and hydrochloric acid and a further quantity of ether until solution was effected. The ethereal extract was shaken several times with concentrated bisulphite solution, and 20 g. of cinnamaldehyde bisulphite compound were obtained corresponding to about half this weight of aldehyde. The ether was washed with

sodium carbonate solution and from this, 4 g. of cinnamic acid were isolated. The ether was now evaporated and the residue distilled in a vacuum. A fraction (165 g.) was obtained, b. p. 150—180°/15 mm., while a second fraction (20 g.) distilled at 220—260°. As this did not crystallise, it was not examined; heat was developed when it was mixed with phenylhydrazine. The main fraction was cooled in a freezing mixture and inoculated with a crystal of styryl methyl ketone. The crystals produced could not be isolated owing to the rapidity with which fusion occurred. The whole of the material was dissolved in alcohol and warmed with phenylhydrazine (80 g.) during 2 hours on the water-bath. The yellow crystals which had separated after 12 hours melted at 158° after being washed with alcohol (yield 100 g.). The mother-liquor was evaporated, and after removal of a second crop of crystals, the thick residue was poured into water, washed with dilute hydrochloric acid, separated from the acid, and steam-distilled. The product in the distillate was extracted with ether and, after removal of the ether, was treated with *p*-nitrobenzoyl chloride in pyridine solution. Addition of water precipitated an oil which immediately solidified and, after recrystallisation from alcohol, the compound melted at 76°. It was compared with and found identical with the corresponding ester of cinnamyl alcohol.

The phenylhydrazone (m. p. 158°) was compared with that obtained from styryl methyl ketone and the identity of the two compounds was proved. After heating in a vacuum, and subsequent distillation, both boiled at 245—250°, and the distillate in each case solidified, yielding, after recrystallisation from spirit, white, crystalline prisms, m. p. 113°, and giving with a nitrite solution the magenta colour which is characteristic of 1 : 5-diphenyl-3-methylpyrazoline.

Action of Cinnamaldehyde on Magnesium Ethyl Iodide.—Magnesium (24 g.; 1 mol.) and ethyl iodide (156 g.; 1 mol.) were allowed to react in anhydrous ether with cooling, and cinnamaldehyde (264 g.; 2 mols.) added as in the experiment with methyl iodide. A brownish-yellow mass was again obtained which was heated during 20 hours on the steam-bath and then decomposed with ice and hydrochloric acid; a bright orange, crystalline material (20 g.) not very soluble in ether then separated which melted at 158° after recrystallisation from spirit and has not yet been identified.

After the ether solution had been washed with bisulphite solution, the ether was removed and the residue thoroughly steam-distilled. From the distillate was extracted an oil, of which a quantity was allowed to react with half its weight of phenylhydrazine. Evolution of heat occurred and after cooling the addition of a little spirit induced the crystallisation of the phenylhydrazone, m. p. 102°, of styryl ethyl ketone. From a second part of the oil cinnamyl

p-nitrobenzoate was obtained by the action of *p*-nitrobenzoyl chloride in pyridine solution.

Action of Trioxymethylene on Magnesium Phenyl Bromide.—The Grignard reagent prepared from bromobenzene (157 g.; 1 mol.) (after separating from unchanged metal) was boiled with trioxymethylene (60 g.; 2 mols.) for 48 hours, a brownish-yellow, viscous mass forming. After decomposition of this material with dilute acid the ethereal extract was shaken with sodium bisulphite solution, 20 g. of the bisulphite compound of benzaldehyde were filtered off, and the ethereal solution remaining was fractionated, 35 g. of benzyl bromide and about 10 g. of diphenyl being obtained.

The author desires to thank the Directors of Boots Pure Drug Co., Ltd., for permission to carry out this work in their laboratories and for the assistance of the Analytical Department of the firm in the analysis of the products obtained.

BOOTS PURE DRUG CO., LTD.,
NOTTINGHAM.

[*Received, July 7th*, 1925.]

CCXCVI.—*Optical Activity and the Polarity of Substituent Groups. Part II. Menthyl Esters of Substituted Acetic Acids.*

By HAROLD GORDON RULE and JOHN SMITH.

POLARITY as applied to substituent effect has, at the present time, at least two distinct meanings in chemistry. On the one hand it is used in the phrase, *general polar effect*, in connexion with a series such as

$$NO_2,\ CN,\ CO_2H,\ Cl,\ Br,\ I,\ OMe,\ H,\ Me,$$

representing the relative influence of the groups on the acidic strength of an aliphatic acid. This sequence has also been traced in the effect of the substituents on velocity of reaction and molecular inductive capacity (see Rule and Paterson, J., 1924, **125**, 2155).

On the other hand, groups are frequently described as positive and negative, either in reference to their directive influence on benzene substitution (Vorländer), or by deduction from Lapworth's principle of induced alternate polarities, or from the electronic theory. On this last basis, it has been shown (Rule, J., 1924, **125**, 1121) that the polarity of substituents, as deduced from the views of J. J. Thomson, leads to the *polar series*

$$NO_2,\ CN,\ CO_2H,\ H,\ Me,\ I,\ Br,\ Cl,\ F,$$

and that this closely corresponds to the relative influence of the

groups on the nitration of benzene, and also on the optical activity of the menthyl esters of *o*-substituted benzoic acids and of certain derivatives of amyl alcohol. Hence the suggestion was advanced that, in general, positive and negative groups influence the rotation of a parent compound in opposite directions, in accordance with the polar series above. The optical activity of other series of compounds was also quoted in support of this suggestion, but very little definite evidence relating to positive groups could be obtained.

In investigations summarised in *Gazzetta*, 1923, **53**, 417, Betti has determined the rotatory powers of a large number of products prepared by condensing an active base with substituted benzaldehydes, with results which show a remarkably close agreement between rotatory powers and the dissociation constants of the corresponding benzoic acids. The measurements, however, all referred to the one solvent, benzene, and to light of one wave-length. Only one positive group (NO_2) is included in the list of substituents examined by Betti, and it is known that solvents may exert a marked preferential effect on the rotation of compounds containing certain substituents, as is seen from the abnormally high rotation of menthyl *o*-nitrobenzoate in benzene solution (Cohen and Armes, J., 1905, **87**, 1190).

In the present communication are recorded the rotatory powers of menthyl esters of the acids $CH_2X{\cdot}CO_2H$, where X = CN,* CO_2H, OH, OMe, and OEt. Determinations were carried out at temperatures between 20° and 95° with the compounds in the homogeneous state, where feasible, and for light of four wave-lengths.

Discussion of Results.

In all cases it was found that the observed rotations could be expressed within the limits of experimental accuracy by a Drude equation of one term. It appears, therefore, that the dispersion is in every case normal and simple. The values of the optical constants and of the dispersion ratio, α_{gr}/α_D, obtained for the acetic derivatives are summarised in Tables I and II.

It will be seen that the substituents affect the rotatory power in the order CN > OH > OMe > OEt > CO_2H and that the values undergo little change with temperature. The values of λ_0^2 vary between 0·0238 and 0·0316 for the homogeneous esters. A number of observations were also made with cyanoacetic ester, glycollic ester, and the hydrogen malonic ester in benzene and chloroform solution. In these cases also the dispersion was apparently simple in character.

* The rotatory power of menthyl cyanoacetate in benzene solution for the D line has been determined by Lapworth (J., 1904, **85**, 43).

Table I.

l-*Menthyl Esters of Acids* $CH_2X{\cdot}CO_2H$ (*Homogeneous State*).

(All rotations are negative in sign.)

X.	CO_2H.		OEt.			
Temp.	59·5°	90·5°	20·5°	37°	61·3°	93·7°
$[K]$	20·72	20·47	21·30	21·39	21·55	21·60
λ_0^2	0·0316	0·0309	0·0262	0·0261	0·0261	0·0269
α_{gr}/α_D	1·184	1·184	1·180	1·182	1·181	1·183
$[M]_D$	158·8°	157·6°	160·6°	161·1°	161·9°	162·9°

X.	OMe.				OH.	CN.
Temp.	20·5°	34·5°	55·5°	93·7°	94·3°	91·3°
$]K]$	23·16	22·95	22·89	22·94	24·34	25·25
λ_0^2	0·0273	0·0278	0·0286	0·0274	0·0312	0·0238
α_{gr}/α_D	1·182	1·181	1·183	1·183	1·184	1·179
$[M]_D$	165·0°	164·4°	163·7°	162·8°	165°	174·1°

Table II.

In Solution (5% *concentration*).*

(All rotations are negative in sign.)

X.	CO_2H.	OH.		CN.	
Solvent.	Benzene.	Benzene.	Chloroform.	Benzene.	Chloroform.
Temp.	18·6°	17·6°	12·3°	19·2°	21·6°
$[K]$	20·14	24·27	26·46	26·20	26·34
λ_0^2	0·0276	0·0255	0·0257	0·0198	0·0334
α_{gr}/α_D	1·185	1·185	1·185	1·181	1·187
$[M]_D$	155·1°	161·2°	180·1°	178·3°	186·9°

* For other concentrations, see Experimental section.

The values of the ratio α_{gr}/α_D for the homogeneous and dissolved compounds remain very constant in the neighbourhood of 1·182.

When the above molecular rotations are compared with rotations recorded in the literature for menthyl esters of other mono-substituted acetic acids, and arranged in order of increasing values, we obtain the following list:

X.	H.	CO_2H.		Me.	OEt.		OMe.		OH.	Br.	Cl.	CN.
$[M]_D$	−157°	158·8°	157·6°	160·2°	160·6°	162·8°	165·0°	162·9°	165·0°	169°	171°	174·1°
Temp.°	*	59·5	90·5	*	*	90	*	90	94·3	*	*	91·3

* Room temperature.

The relative effect of the substituents on optical activity in this case is therefore,

I. $CN > Cl > Br > OH > OMe > OEt > Me > CO_2H > H.$

This corresponds closely with the general polar effect of the groups, as may be seen by comparison with series II, representing

their influence on molecular inductive capacity (see Rule and Paterson, *loc. cit.*), and with series III, representing their influence on the acidity of acetic acid.

II. $CN > CO_2H(?) > OH > Cl > Br > (OMe,OEt) > CO_2H(?) > Me > H$.
III. $CN > CO_2H > Cl > Br > OMe > OH > H > Me$.

The position of the carboxyl group in series II is somewhat doubtful, formic acid having a high inductive capacity and acetic and propionic acids low values.

The analogy between the effect of substitution on optical activity and acidic strength which has previously been drawn by Betti (*loc. cit.*) is therefore confirmed and amplified. Among the menthyl esters of acetic acid there is no indication of positive groups affecting the rotatory power in an opposite sense to negative groups, as is the case with the benzoates.

It may therefore be concluded that the two types of group effect previously observed, namely, the general effect visible in inductive capacity, acidic strength and chemical reactivity, and the polar effect, as deduced from the electronic theory and traceable in benzene substitution and electromagnetic rotation, are both to be found in optical activity.

Experimental.

The menthol used was specially purified material, with a rotation of $[\alpha]_D^{18°}$ −49·50° in 5% ethyl-alcoholic solution.

The ethoxy- and methoxy-acetic esters were prepared by the method described in U.S. Pat. 836914, and D.R.-P. 191547, in which, however, no mention is made of rotatory power.

l-*Menthyl methoxyacetate* was prepared from the corresponding acid chloride, menthol and pyridine, in benzene solution. On being fractionated under reduced pressure, it was obtained as a colourless, odourless liquid, b. p. 141°/16 mm. After the second fractionation, a repetition of the process produced no change in rotatory power. It has not previously been recorded that *l*-menthyl methoxyacetate is a solid of m. p. 18° (Found: C, 68·4; H, 10·45. Calc. for $C_{13}H_{24}O_3$, C, 68·4; H, 10·5%).

l-*Menthyl ethoxyacetate*, prepared in a similar way, boiled at 150°/18 mm. It also was odourless (Found: C, 69·4; H, 10·7. $C_{14}H_{26}O_3$ requires C, 69·4; H, 10·7%).

l-*Menthyl glycollate* is also described in the same brief manner in the patent specification, D.R.-P. 136411. It was prepared by heating glycollic acid (3 mols.) with menthol (1 mol.) on a steam-bath for 14 hours, dry hydrogen chloride being passed through

the mixture for 10 minutes in each hour. The cooled mass was extracted with ether, washed, and dried. After removal of ether, the menthol was distilled under diminished pressure (oil-bath at 130°). The resulting dark solid was finally recrystallised from light petroleum until of constant rotation. The pure ester crystallises in long, white needles, m. p. 87·5° (above specification quotes 87°). It is moderately soluble in benzene and readily soluble in chloroform (Found: C, 67·3; H, 10·3. Calc. for $C_{12}H_{22}O_3$, C, 67·3; H, 10·3%).

l-*Menthyl cyanoacetate* was obtained from ethyl cyanoacetate by the method of Lapworth (*loc. cit.*).

l-*Menthyl Hydrogen Malonate.*—Dimenthyl malonate was first prepared by a modification of the method of Hilditch (J., 1909, **95**, 1571), using, however, pyridine as condensing agent.

The pure diester had a rotation of $\alpha^{20°}_{5461} = -9·36°$ (4·98% chloroform solution; $l = 2$). Hall (J., 1923, **123**, 109) quotes $-9·32°$.

In the preparation of menthyl hydrogen malonate, the diester (22 g.), dissolved in 96% alcohol (1 litre), was hydrolysed at 0° by gradual addition of the requisite amount of sodium ethoxide in alcoholic solution. On recrystallisation from ethyl acetate, it was obtained in plates, m. p. 58·5—59° (Found: C, 64·4; H, 9·1. $C_{13}H_{22}O_4$ requires C, 64·5; H, 9·1%).

Densities and Rotatory Powers of the Esters in the Homogeneous State.

Rotations generally refer to a 50 mm. tube (* indicates 100 mm.) and are all negative in sign.

l-Menthyl methoxyacetate.

$D^{t°}_4$	1·0136 at 20°; 0·9964 at 40·3°; 0·9807 at 60°; 0·9638 at 80°.
α_D	73·33°* at 20·5°; 72·07°* at 34·5°; 35·31° at 55·5°; 34·13° at 93·7°.
α_{ye}	76·47°* at 20·5°; 75·14°* at 34·5°; 36·82° at 55·5°; 35·65° at 93·7°.
α_{gr}	86·70°* at 20·5°; 85·14°* at 34·5°; 41·78° at 55·5°; 40·40° at 93·7°.
α_{vl}	144·32°* at 20·5°; 142·02°* at 34·5°; 69·74° at 55·5°; 67·19° at 93·7°.

l-Menthyl ethoxyacetate.

$D^{t°}_4$	0·9545 at 20°; 0·9379 at 40·6°; 0·9242 at 58°; 0·9070 at 79·2°.
α_D	63·31°* at 20·5°; 31·31° at 37°; 30·89° at 61·3°; 30·16° at 93·7°.
α_{ye}	65·96°* at 20·5°; 32·70° at 37°; 32·28° at 61·3°; 31·50° at 93·7°.
α_{gr}	74·68°* at 20·5°; 37·01° at 37°; 36·48° at 61·3°; 35·70° at 93·7°.
α_{vl}	124·18°* at 20·5°; 61·41° at 37°; 60·57° at 61·3°; 59·31° at 93·7°.

l-Menthyl glycollate.

$D^{t°}_4$ 0·9469 at 94·3°.

At 94·3° $\alpha_D = 36·50°$; $\alpha_{ye} = 38·09°$; $\alpha_{gr} = 43·23°$; $\alpha_{vl} = 72·71°$.

l-Menthyl cyanoacetate.

$D^{t°}_4$ 0·9406 at 91·3°.

At 91·3° $\alpha_D = 36·71°$; $\alpha_{ye} = 38·28°$; $\alpha_{gr} = 43·28°$; α_{vl} (not determined owing to slight yellow colour of liquid).

l-Menthyl hydrogen malonate.

$D_{4^\circ}^{t^\circ}$ 1·0238 at 59·5°; 1·0008 at 90·5°.
At 59·5° $a_D = 33·61°$; $a_{ye} = 35·07°$; $a_{gr} = 39·89°$; $a_{vl} = 67·01°$.
At 90·5° $a_D = 32·60°$; $a_{ye} = 33·96°$; $a_{gr} = 38·59°$; $a_{vl} = 64·86°$.

Rotatory Powers of the Esters in Solution.

Ester.	Solvent.	Temp.	G. of ester in 100 c.c.	a obs. ($l = 2$). a_D.	a_{ye}.	a_{gr}.	a_{vl}.
Glycollate	Benzene	17·6°	5·004	7·54°	7·89°	8·94°	14·76°
,,	Chloroform	12·3	5·003	8·42	8·77	9·98	16·49
,,	,,	12·3	16·192	27·06	—	—	—
Cyanoacetate	Benzene	19·2	5·002	8·00	8·38	9·45	15·40
,,	,,	17·0	11·36	4·51	(50 mm. tube)		
,,	Chloroform	21·8	5·004	8·39	8·81	9·96	16·83
,,	,,	21·0	14·981	6·21	(50 mm. tube)		
Hydrogen malonate	Benzene	18·8	4·914	6·30	6·56	7·47	12·41
,, ,,	,,	19·0	20·08	12·88	(1 dcm. tube)		

Specific Rotatory Powers of Esters in Homogeneous State.

l-Menthyl methoxyacetate.

t.	$D_{4^\circ}^{t^\circ}$.	$[a]_D$.	$[a]_{ye}$.	$[a]_{gr}$.	$[a]_{vl}$.
20°	1·0136	−72·35°	−75·49°	−85·56°	−142·39°
40	0·9970	72·04	74·92	84·93	141·95
60	0·9805	71·72	74·78	84·89	141·68
80	0·9638	71·63	74·83	84·87	141·32
90	0·9555	71·47	74·87	84·87	141·14

l-Menthyl ethoxyacetate.

20	0·9545	−66·35	−69·10	−78·29	−130·20
40	0·9383	66·62	69·62	78·76	130·66
60	0·9224	66·90	70·05	79·18	131·37
80	0·9063	67·19	70·30	79·54	132·05
90	0·8983	67·30	70·35	79·69	132·38

	t.	$D_{4^\circ}^{t^\circ}$.	$[a]_D$.	$[a]_{ye}$.	$[a]_{gr}$.	$[a]_{vl}$.
l-Menthyl hydroxyacetate	94·3°	0·9469	−77·09°	−80·48°	−91·26°	−153·6°
cyanoacetate	91·3	0·9406	78·06	81·39	92·03	—
hydrogen malonate	59·5	1·0238	65·65	68·51	77·75	130·9
,, ,,	90·5	1·0008	65·14	67·86	77·11	129·6

Specific Rotatory Powers of l-*Menthyl Esters in Solution.*

Ester.	Solvent.	G. of ester in 100 c.c.	Temp.	$[a]_D$.	$[a]_{ye}$.	$[a]_{gr}$.	$[a]_{vl}$.
Glycollate	Benzene	5·004	17·6°	75·34°	78·84°	89·33°	147·5°
,,	Chloroform	5·003	12·3	84·15	87·64	99·74	164·8
Cyanoacetate	Benzene	5·002	19·2	79·97	83·77	94·46	153·9
		11·365	17·0	79·37			
,,	Chloroform	5·004	21·8	83·83	88·03	99·52	168·2
		14·981	21·0	82·91			
Hydrogen malonate	Benzene	4·914	18·8	64·10	66·74	76·00	126·3
		20·078	19·0	64·14			

Molecular Rotations of Esters.

Substituent group.	Temp.	Mol. rotations. Liq. state.	Mol. rotations. Solution.	Substituent group.	Temp.	Mol. rotations. Liq. state.	Mol. rotations. Solution.
CO_2H	18·8°	—	155·1°*	OMe	60°	163·5°	
	59·5	158·8°			80	163·3	
	90·5	157·6			90	162·9	
OEt	20	160·6		OH	12·3	—	180·1†
	40	161·2			17·6	—	161·2*
	60	161·9			94·3	165·0	
	80	162·6		CN	19·2	—	178·3*
	90	162·8			21·8	—	186·9†
OMe	20	165·0			91·3	174·1	
	40	164·2					

Solvent: * benzene, † chloroform.

In conclusion, the authors desire to thank the Earl of Moray Fund for a grant which has covered most of the expenses involved.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF EDINBURGH. [*Received, July 4th,* 1925.]

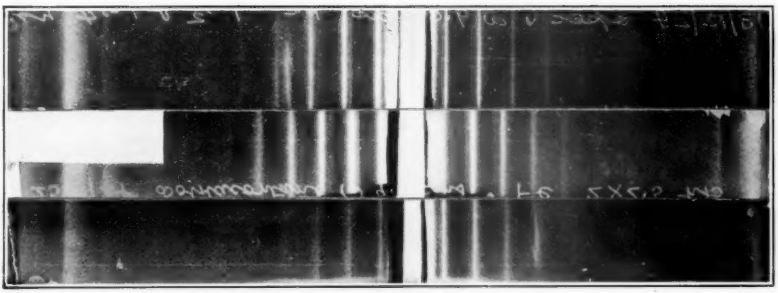
CCXCVII.—X-*Rays and the Constitution of the Hydrocarbons from Paraffin Wax.*

By STEPHEN HARVEY PIPER, DENNIS BROWN, and STANLEY DYMENT.

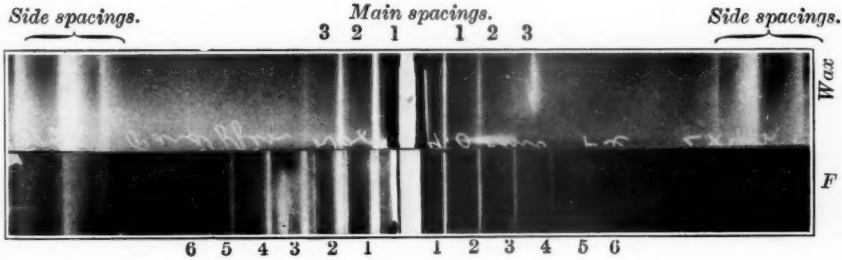
SINCE the distance apart of the main cleavage planes of the crystals of long-chain compounds has a definite relation to the length of the constituent molecules (Müller and Shearer, J., 1923, **123**, 2043, 3153; this vol., pp. 592, 600), *X*-ray examination of the spacing of such planes of unknown crystals may give important information as to the nature of the structural molecules. The nature of the hydrocarbons composing paraffin wax is unknown, although it has been conjectured, on slender evidence, that they are higher members of the normal methane series. It was hoped that *X*-ray examination of the crystals of the individual hydrocarbons would throw some light on their constitution.

Origin of the Hydrocarbons.—The seven solid hydrocarbons, an investigation of which forms the subject of this communication, were isolated by Prof. Francis and his students from Scotch paraffin wax by long-continued fractionation in high vacua (J., 1922, **121**, 1529). These authors believed that 80% of the original material was composed of seven hydrocarbons, boiling at constant temperature; and their opinion that these hydrocarbons were not mixtures was strengthened by their later work (*loc. cit.*, p. 2804), which showed

FIG. 1.



* *Dotriacontane.*



[*To face p.* 2194.]

that, on oxidation of each fraction by air, the small amounts of hydrocarbon which escaped this process were identical in every case with the original material.

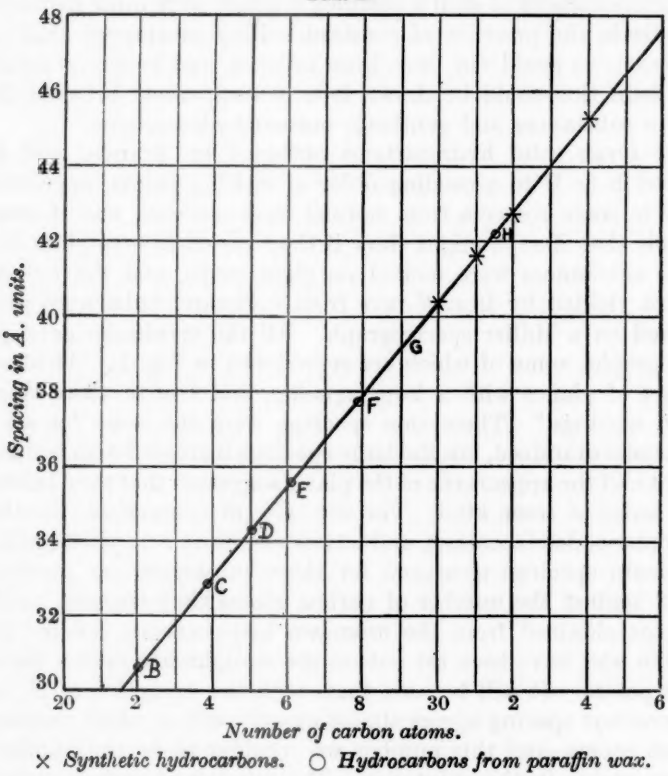
Krafft (*Ber.*, 1907, **40**, 4779) isolated eighteen hydrocarbons by fractionation of Saxon paraffin wax in the " vacuum of the cathode rays," and identifying these with those he had synthesised from materials of known constitution, drew the conclusion that the wax was composed of a large number of the higher normal members of the paraffin hydrocarbons. Francis has pointed out, however, that five fractionations of such a complex mixture were quite insufficient to indicate the presence of constant-boiling substances, that pure hydrocarbons could not have been isolated, and hence no satisfactory deduction could be drawn from a comparison between these impure substances and synthetic normal hydrocarbons.

The seven solid hydrocarbons obtained by Francis, and here lettered B to H in ascending order of melting points, appeared to differ in some respects from normal hydrocarbons, and it seemed possible that *X*-rays might show if they varied in crystalline form.

The substances were melted on glass strips, and the reflection spectra yielded by iron *K*-rays from a Shearer tube were photographed on a Müller spectrograph. All the specimens gave good photographs, some of which are reproduced in Fig. 1. All showed one set of planes with a large spacing, and two or three smaller " side spacings." These side spacings were the same for all the substances examined, but the large spacings increased with molecular weight and the appearance of the plates suggested that they belonged to a series of some kind. For the sake of comparison, synthetic triacontane, dotriacontane, and tetratriacontane were photographed. The main spacings measured for these substances are plotted in Fig. 2 against the number of carbon atoms they contain, and the spacings obtained from the unknown hydrocarbons isolated from paraffin wax have been set out on the straight line drawn through these points. It will be seen that, with the exception of H, each hydrocarbon spacing agrees almost exactly with a whole number of carbon atoms, and this number we consider to be the number of carbon atoms in the substance. The number of carbon atoms so obtained does not, however, in the cases of B, E, F, and G agree with the value deduced from the molecular weight determinations and published by Francis (J., 1922, **121**, 1531). In Table I, columns 3 and 4, the two sets of values are compared. We considered that our graph showed definitely the presence of the seven different hydrocarbons in column 3, and our belief in the method was strengthened by a measurement made on a hydrocarbon synthesised by the electrolysis of what was believed to be pure stearic acid, and which

therefore should have been tetratriacontane. The photograph of this hydrocarbon, however, only showed the lines corresponding to dotriacontane, and further examination proved that the specimen actually was this hydrocarbon. An investigation of the stearic acid used in the preparation showed the presence of a quantity of palmitic acid; consequently the reaction must have taken place between the radicals of palmitic and stearic acids rather than of stearic acid only. A specimen of a hydrocarbon prepared by the

FIG. 2.



× *Synthetic hydrocarbons.* ○ *Hydrocarbons from paraffin wax.*

same method from carefully purified stearic acid gave the spacing expected for tetratriacontane. A redetermination of the molecular weights of the hydrocarbons from the paraffin wax was obviously desirable, and this was undertaken by Dr. Christie of the Chemical Department, to whom our best thanks are due.

The difficulty of obtaining trustworthy results by the Beckmann ebullioscopic method is well known, in spite of the fact that, a definite experimental procedure always being adopted, very

concordant observations may be made. Using benzene as a solvent, Prof. Francis (*loc. cit.*) had obtained data agreeing among themselves in many cases to 1%. In order to vary the procedure, Dr. Christie employed the newer method of Menzies and Wright (*J. Amer. Chem. Soc.*, 1921, **43**, 2314), which is stated by these authors to give more accurate results. The constant for benzene, 26·1, given by them gave too low a value for the molecular weight of dotriacontane, which was regarded as a standard; the value 26·67 has therefore been used throughout these determinations, which in all cases were carried out under precisely similar conditions.

The mean molecular weight determined for dotriacontane was 452 in both chloroform and benzene. The calculated value is 450 and in each solvent individual determinations did not differ by as much as 1%.

Fraction B. The old value 325 was confirmed, four determinations in benzene giving 321 with a maximum variation of just over 1%. $C_{23}H_{48}$ requires *M*, 324.

Fraction C. The previous value was 332. Using benzene as a solvent, the mean of eight determinations by the new method was found to be 336 with an extreme variation of just under 2%. In chloroform the mean of seven determinations gave 338 with a variation of about 1%. $C_{24}H_{50}$ requires *M*, 338.

Fraction D. Only a small quantity of this fraction was available. The old value was 358, but in benzene *M* was now found to be distinctly higher, *viz.*, 368 with a maximum variation of about 1%. This appears to be $C_{26}H_{54}$ (*M*, 366).

Fraction E. Old determination 394. The mean of eight observations in benzene was 369, and of four in chloroform 366, the variation being about 1%. This agrees with the molecular weight of $C_{26}H_{54}$, in which case E is isomeric with D, although the photographs are quite different.

Fraction F. Old value 419. The mean of eight observations in benzene was 390, and of nine in chloroform 396. Probably the substance is $C_{28}H_{58}$ (*M*, 394).

Fraction G. Old value 449 corresponding to $C_{32}H_{66}$. The photographs of G and of dotriacontane, reproduced in Fig. 1, are quite different. Three measurements in benzene with the new apparatus gave *M* 407. Three more by another investigator gave the same mean value. Three in chloroform gave 408, by the other observer 410. This hydrocarbon appears to be $C_{29}H_{60}$ (*M*, 408).

Fraction H. Previous value 434. Five determinations of *M* in benzene now gave a mean value of 443, and it is considered probable that this hydrocarbon is $C_{31}H_{64}$ (*M*, 436). It certainly is not dotriacontane (see Fig. 1).

These new magnitudes are shown in Table I, column 5.

TABLE I.

Substance.	Spacing in Å. units.	n, the number of carbon atoms in the molecule. Authors.	Beckmann.	Menzies and Wright.
Synthetic $C_{30}H_{62}$	40·4			
„ $C_{32}H_{66}$	42·7			
„ $C_{34}H_{70}$	45·3			
B	30·6	22	23	23
C	32·86	24	24	24
D	34·3	25	25	26
E	35·6	26	28	26
F	37·75	28	30	28
G	39·45	29	32	29
H (melted)	42·2	31·5	31	31
H (pressed)	42·9	31	31	31
Synthetic $C_{31}H_{64}$ (melted)	41·6			
„ $C_{31}H_{64}$ (pressed)	43*			

* Müller and Saville, this vol., p. 600.

In the case of hydrocarbons C, E, F, and G the number of atoms deduced from Dr. Christie's observations agrees with our estimate, for D there is agreement with the Beckmann value, whilst B and H differ. We give reasons below for considering that our measure of the spacing of hydrocarbon H corresponds to a value of n of 31; and we believe that the hydrocarbon B is $C_{22}H_{46}$, or at any rate contains this substance. A difference of one carbon atom in the chains of two of these hydrocarbons will separate the third-order lines in the photographs by about 0·33 mm. (see Fig. 1, H and dotriacontane), and as it is possible to measure a good plate to 0·01 mm. it is almost impossible to confuse two different substances. As is mentioned below, an absolutely uniform method of mounting the specimens is necessary.

We consider that the photographs show that the hydrocarbons obtained from paraffin wax are identical in constitution with the synthetic normal hydrocarbons for the following reasons.

(1) If the chains differed in nature, the unknown hydrocarbon line would not coincide in slope with the line on which the synthetic hydrocarbons lie.

(2) The intensity of the lines falls off uniformly with increasing order. There cannot be, therefore, a side chain attached to the main chain (Shearer, this vol., p. 597). If the end groups differed, then one line would lie above the other, the larger end groups being on the upper line. As the spacing measurement gives the minimum number of carbon atoms in the substance, the general agreement between this number obtained from the photographs and that deduced from the molecular-weight determinations makes it certain

that there are no more carbon atoms in the substances than are accounted for in the chains.

Whilst these experiments were in progress Müller and Saville completed a series of measurements of the spacings of the normal paraffin hydrocarbons, and found that the lower members had two modifications, A and B (this vol., p. 600). A comparison between our values and theirs shows differences much greater than the possible experimental error. This discrepancy is due to a difference in technique; Müller and Saville pressed crystal flakes on a glass plate, whilst we melted our specimens on the glass. Our measurements do not correspond to either the A or B modifications, from which we conclude that the lattice has been distorted by the melting on glass. We have been able to verify this by a measurement of hentriacontane, most kindly given to us by Dr. Müller. This substance when melted gives a spacing that falls on the line given by our other synthetic hydrocarbons; it is plotted in Fig. 2. The spacing we found for the same substance when its crystals were pressed on glass was much higher. An investigation into this behaviour is nearly completed and will be discussed in a separate communication. It is sufficient to state here that uniform treatment of the substances under investigation gives consistent results. Hydrocarbon H, when its crystals are pressed on glass, gives a spacing which agrees with that obtained by Müller and Saville (*loc. cit.*) for hentriacontane (see Table I). This substance is therefore hentriacontane. It remains to account for the anomalous value given by the melted substance.

Mixed Substances, melted together.—A photograph of crude paraffin wax is shown in Fig. 1 above that of fraction F. The lines of the two substances coincide—a remarkable fact, since fraction F only furnishes about 16% of the mixture; in fact it is not the most plentiful constituent. Measurement of the lines shows a very slight difference between the spacings, but as we have not been able to obtain more than three orders from the wax this difference may be partly experimental error. In general, however, we find that a mixture containing F shows only the F lines, slightly modified, provided the mixture is *melted* on the glass. Other mixtures, when melted together, usually yield modified lines of the longer chain, but if crystals of the two substances are pressed on the mounting the lines of both photograph unaltered. We consider that the anomalous spacing given by the melted specimen of hydrocarbon H may be ascribed to the presence of some impurity, too small in amount to show its lines in the photograph of the pressed substance. It will be noticed that the redetermination of the molecular weight of this substance does not give very satisfactory results; a similar

explanation will account for this. We believe the other hydrocarbons supplied by Prof. Francis to be fairly pure; the lines obtained fall very exactly on the normal hydrocarbon curve. Certainly those preceding and following F are not contaminated by this hydrocarbon to any appreciable extent. In the present state of our knowledge of the behaviour of mixed substances when examined by this method it is dangerous to generalise, but we believe that a normal spacing is at least an indication of a pure substance.

These experiments were carried out with the aid of a grant from the University Colston Research Society.

THE UNIVERSITY, BRISTOL. [*Received, July 15th*, 1925.]

CCXCVIII.—*Constituents of* Myoporum laetum, *Forst* (*the "Ngaio"*). *Part I.*

By FREDERICK HENRY MCDOWALL.

THE first section of this paper deals with the aqueous extracts of various parts of the "ngaio" tree. Mannitol is present in the leaves to the extent of 0·2% (calculated on the weight of green leaves used), in the berries, which contain formic acid also, and in the wood to the extent of 0·25%.

The second section deals with the essential oil, 86% of which consists of an oxygenated sesquiterpene ketone, $C_{15}H_{22}O_3$, for which the author proposes the name "*ngaione*" (pronounced "ny-one") after the Maori name for the tree. Ngaione is characterised by its crystalline p-*nitrophenylhydrazone* and by its *semicarbazone*. The substance contains only one carbonyl group, and no methoxy- or methylenedioxy-group. It is reduced by sodium and alcohol to a secondary alcohol, *ngaiol*, which forms a monoacetate and a monomethyl ether. It is concluded that alcoholic hydroxyl groups are absent and that the molecule contains two separate oxide rings, since the presence of an organic peroxide ring would probably render the substance unstable (compare ascaridole, *loc. cit.*). The molecular refraction indicates that ngaione contains two ethylenic linkings. Since these remain unattacked by sodium and alcohol, they cannot be in the αβ-position to the carbonyl group, or conjugated with each other. Ngaione is thus probably an open-chain diolefinic ketone.

A solid paraffin hydrocarbon, $C_{32}H_{66}$ or $C_{34}H_{70}$, is also present in the essential oil.

Maiden (J., 1899, **55**, 665) isolated a resin from the exudations of *Myoporum platycarpum*, R. Br. No similar exudations occur on

Myoporum laetum, Forst. None of the species of *Myoporum* has been examined for essential oil.

Only a few substances of a like nature to ngaione have been isolated from essential oils. Apart from the well-known cineole, these are: Ascaridole, $C_{10}H_{16}O_2$ (Nelson, *J. Amer. Chem. Soc.*, 1911, **33**, 1404; Wallach, *Annalen*, 1912, **392**, 59); kessyl alcohol, $C_{14}H_{24}O_2$ (Bertram and Gildemeister, *Arch. Pharm.*, 1890, **228**, 483); calameone, $C_{15}H_{26}O_2$ (Soden and Rojahn, *Chem. Zentr.*, 1901, I, 1893; Thoms and Beckstrom, *Ber.*, 1901, **34**, 1021; 1902, **35**, 3187); kaempferia ketone, $C_{24}H_{28}O_4$ (Goulding and Roberts, J., 1915, **107**, 314); daucol, $C_{15}H_{26}O_2$ (Richter, *Arch. Pharm.*, 1908, **247**, 391); and dicitronelloxide, $C_{20}H_{34}O$ (Spornitz, *Ber.*, 1904, **47**, 478). Carlina oxide, $C_{13}H_{10}O$ (Semmler and Ascher, *Ber.*, 1909, **42**, 2355), is an aromatic compound, and elsholtzione, $C_{10}H_{14}O_2$ (Asahina and Murayama, *Arch. Pharm.*, 1914, **252**, 435; Asano, *J. Pharm. Soc. Japan*, 1919, **454**, 999), a furan derivative. Of the terpenic substances, the only one to which a constitution has been assigned is ascaridole (Wallach, *loc. cit.*). Many of these compounds, like ngaione, have a relatively high density.

EXPERIMENTAL.

Non-volatile Aqueous Extract.

(a) *Extraction of Leaves.*—The green leaves, after the essential oil had been removed by steam distillation, were extracted with water, and the filtrate was evaporated in a vacuum at 60°. The green residue gave to chloroform, ether, benzene, and light petroleum only a small quantity of colouring matter, but a hot alcoholic extract deposited, on cooling, white needles of mannitol, $[\alpha]_D$ (5% solution in presence of borax) +20·7°. After four crystallisations, this, alone or mixed with a genuine specimen, melted at 164—165°. On acetylation, it gave hexa-acetyl mannitol, m. p. 120°. The yield of mannitol was 10 g. from 5 kilo. of green leaves.

(b) *Extraction of Berries.*—The aqueous extract of the crushed berries was freed from tannin with lead acetate, boiled with animal charcoal, and evaporated in a vacuum. The residue yielded mannitol on extraction with hot alcohol.

(c) *Extraction of Wood.*—The residue from the aqueous extract of 1 kilo. of undried sawdust gave, when treated with alcohol, 2·5 g. of crude mannitol.

The Essential Oil.

The leaves and terminal branchlets (80 kilo. at a time) were distilled with superheated steam, 120 litres of distillate generally proving sufficient for complete extraction. The aqueous layer was

siphoned from the underlying layer of oil, and was then extracted twice with light petroleum. The yields ranged from 0·12% to 0·30%, varying with season and sample. The oil was cooled to −20° and the solid that separated (yield 0·01% of the crude oil) was recrystallised six times from hot absolute alcohol; m. p. 62—63° (Found: C, 85·4; H, 14·9; *M*, cryoscopic and ebullioscopic in benzene, 470. $C_{32}H_{66}$ requires C, 85·2; H, 14·8%; *M*, 450. $C_{34}H_{70}$ requires C, 85·3; H, 14·7%; *M*, 479). The substance is therefore a paraffin hydrocarbon of probable formula $C_{32}H_{66}$ or $C_{34}H_{70}$. The literature records the isolation of several similar compounds from essential oils (compare especially rose oil, *Bull. Soc. chim.*, 1904, **31**, 934).

The crystals were easily soluble in benzene, ether, chloroform, etc., slightly soluble in hot alcohol, but practically insoluble in cold alcohol. They were unaffected by bromine water or bromine in ether and were stable towards permanganate.

The clear oil, after removal of stearoptene, was of a reddish-brown colour and had a sweet malt-like odour; $d_{20^\circ}^{20^\circ}$ 1·0203; $[\alpha]_D$ −26·54°, $n_D^{20^\circ}$ 1·4823, saponification value, by direct titration after 2 hours' heating with alcoholic potash, 17·9. It was soluble in half its volume of 90% alcohol and in 4½ volumes of 70% alcohol. No seasonal variation was observed in the values of the constants. No nitrogen- or sulphur-containing substances were present (Found for crude oil: C, 71·5; H, 9·5%). The high density and high oxygen content seemed to indicate the presence of phenolic compounds, but treatment with caustic soda gave a yield of only 0·41% of phenols, and a methoxyl determination showed the absence of methylated phenols. From the low saponification value it was evident that lactones or esters were not present to any appreciable extent. The oil yielded no trace of aldehyde or ketone sodium bisulphite compound.

Repeated distillation of 850 g. gave the following fractions: up to 200°, 2 g.; 200—268° (in seven fractions), 22 g.; 160—166°/27 mm., 6 g.; 166—176°/27 mm., 8 g.; 176—182°/27 mm., 8 g.; 182—183°/27 mm., 730 g.; 183—189°/27 mm., 20 g.; non-volatile residue, 30 g.; loss, 24 g.

Ngaione.—The main fraction, b. p. 182—183°/27 mm., constituting 86% of the oil, is the only one so far examined. It was divided into three portions by repeated distillation, the refractive index of the last drop of liquid issuing from the condenser being used as a means of division in the absence of a boiling-point range. The middle portion (600 g.) was a lemon-yellow oil with a faint odour, $d_{20^\circ}^{20^\circ}$ 1·0276, $[\alpha]_D$ −26·20°, $n_D^{20^\circ}$ 1·4804. The substance is profoundly altered by distillation at ordinary pressures; b. p. 300°,

n_D of distillate, 1·4900. Duplicate analyses indicated very consistently the formula $C_{16}H_{24}O_3$ (see, however, analyses of crystalline derivatives and of purified ketone, which agree closely with $C_{15}H_{22}O_3$) (Found for three separate samples: C, 72·6, 72·3, 72·6; H, 9·3, 9·3, 9·0; *M*, cryoscopic in benzene and ethylene bromide, 250. $C_{16}H_{24}O_3$ requires C, 72·7; H, 9·2%; *M*, 264. $C_{15}H_{22}O_3$ requires C, 71·9; H, 8·9%; *M*, 250).

The p-*nitrophenylhydrazone* was prepared by heating a filtered solution of 1 g. of *p*-nitrophenylhydrazine in 7 g. of alcohol and 7 g. of glacial acetic acid with 1·8 g. of the substance for 1 hour on the water-bath. After 24 hours, the emulsion produced on addition of water was extracted with ether. The extract was washed with dilute sulphuric acid and with sodium carbonate solution, dried, and the solvent evaporated over sulphuric acid. The residue of large, bright yellow tablets was washed with cold alcohol and recrystallised from warm alcohol; m. p. 103° (Found: C, 65·5, 65·4; H, 7·4, 7·1. $C_{21}H_{27}O_4N_3$ requires C, 65·4; H, 7·1. $C_{22}H_{29}O_4N_3$ requires C, 66·1; H, 7·3%).

The ketone (6 g.) and thiosemicarbazide (2·2 g.) were heated together in 30 c.c. of 63% alcohol on the water-bath for 12 hours; the alcohol was then evaporated, and the residue extracted with ether. From the extract a thick, reddish-brown oil, which could not be crystallised, was obtained (Found: S, 6·6. *Ngaione thiosemicarbazone*, $C_{16}H_{25}O_2N_3S$, requires S, 9·9%). The substance was treated in alcoholic solution with silver nitrate (2 equivs. were necessary for complete precipitation), and the yellow *silver* salt was filtered, washed with alcohol and ether, and dried (Found: Ag, 32·7. $C_{16}H_{24}O_2N_3SAg$ requires Ag, 25·0%. The double salt with silver nitrate requires Ag, 35·9%). The solid was therefore probably an impure double salt. Ngaione thiosemicarbazone was recovered from the silver salt as a thick syrup which could not be crystallised.

The silver compound (6·5 g.) was steam-distilled with excess of phthalic anhydride; the oil extracted from the distillate with light petroleum (yield 1·8 g.) had b. p. 185°/29 mm. (188° corr.), $d_{20°}^{20°}$ 1·0273, $n_D^{20°}$ 1·4794, $[R_L]_D$ 69·10. $C_{15}H_{22}O_3$, $\overline{=}_2$, requires $[R_L]_D$ 69·43 (Found: C, 71·9; H, 8·9. $C_{15}H_{22}O_3$ requires C, 71·9; H, 8·9%). This analysis and that of the *p*-nitrophenylhydrazone definitely establish the formula of ngaione as $C_{15}H_{22}O_3$.

Ngaione slowly reduced ammoniacal silver nitrate and Fehling's solution, more rapidly in presence of alcohol. It did not affect Schiff's reagent. In alcoholic solution it gave a bright green fluorescence with *m*-phenylenediamine hydrochloride, the colour being much more pronounced than that due to alcohol alone. It

did not, however, give a solid bisulphite compound under all conditions tried (compare kaempferia ketone, *loc. cit.*).

In an oximation experiment 63% of ngaione was converted in ½ hour and 76% in 2½ hours (Bennet, *Analyst*, 1909, 14). An alcoholic solution of ngaione (1 mol.) was heated with hydroxylamine hydrochloride (1¼ mols.) and sodium hydroxide (1⅛ mols.) on the water-bath for 5 hours. After removal of alcohol in a vacuum water was added, and the heavy oil extracted with ether. By distillation under reduced pressure the *oxime* was isolated as a lemon-yellow, viscous oil which could not be crystallised; b. p. 201°/27 mm., $d_{20°}^{20°}$ 1·0640, $[\alpha]_D$ (in 10% solution in chloroform) −13·51°, $n_D^{23°}$ 1·5008, $[R_L]_D$ 73·37. *Ngaione oxime*, $C_{15}H_{23}O_3N$, requires $[R_L]_D$ 73·74 (Found: C, 67·6; H, 8·6; N, 5·5. $C_{15}H_{23}O_3N$ requires C, 67·9; H, 8·7; N, 5·3%). The carbanilide of the oxime is a syrup.

The *semicarbazone* was prepared in aqueous alcoholic solution. After the mixture had been allowed to stand for a fortnight, water was added, and the precipitated solid dried on porous tile. No suitable crystallising medium could be found, the substance being extremely soluble in all solvents. Purified by reprecipitation several times from alcohol by the addition of water, it melted at 120—122° (decomp.) (Found: C, 62·9; H, 8·5. $C_{16}H_{25}O_3N_3$ requires C, 62·5; H, 8·2%).

The phenylhydrazone and *p*-bromophenylhydrazone are liquid. The substance would not form a semioxamazone even in the undiluted state at 170°; and under the conditions laid down by Doebner (*Ber.*, 1894, **27**, 852) as applicable to all aldehydes, it failed to yield a β-naphthacinchoninic acid. It also did not combine with freshly distilled pyruvic acid in presence of caustic soda (Lubrzynska and MacLean, *Chem. Zentr.*, 1914, 561), neither did it give a cyanoacetic acid compound. The failure to react with these aldehyde reagents, the slow nature of its combination with hydroxylamine, thiosemicarbazide, etc., the inertness towards sodium bisulphite and semioxamazide, all lead to the conclusion that the substance is a ketone. This conclusion is supported by the fact that an acid of the same number of carbon atoms cannot be obtained, either by the use of oxidising agents or through dehydration of the oxime and subsequent hydrolysis. The reducing action towards Fehling's solution and silver nitrate is very sluggish, and, moreover, it does not appear to be due to the presence of the carbonyl group alone, since the purified alcohol (see below) also is slowly oxidised.

With boiling acetic anhydride ngaione is partially converted into the enolic acetate (saponification value 73. $C_{15}H_{21}O_2 \cdot O \cdot CO \cdot CH_3$

requires 192). Ngaione decolorised bromine water very slowly; bromine in ether was rapidly absorbed, but the product was tarry.

Ngaiol.—With sodium (8 times the theoretical quantity) and absolute alcohol, ngaione formed an alcohol, *ngaiol* (yield 86%), which was purified through the acid phthalate, the usual proportions of benzene and phthalic anhydride being heated with the oil on a water-bath for 120 hours. The slowness of the reaction indicates the presence of a secondary alcohol, confirming the conclusion that the original substance is a ketone (combination takes place more rapidly without solvent at 130—140°, but is accompanied by a certain amount of racemisation). Ngaiol was thus obtained as a lemon-yellow oil with a faint sweet odour, b. p. 191—192°/29 mm. (195—196° corr.), $d_{20^\circ}^{20^\circ}$ 1·0163, $[\alpha]_D$ −25·00°, $n_D^{20^\circ}$ 1·4784, $[R_L]_D$ 70·28. $C_{15}H_{24}O_3$, $\overline{2}$, requires 70·94 (Found: C, 71·3; H, 9·8; M, cryoscopic in benzene, 260. $C_{15}H_{24}O_3$ requires C, 71·4; H, 9·6%; *M*, 252). These figures further check the formula suggested for the ketone. No trace of a pinacol was observed.

Treatment with the calculated quantity of chromic oxide in glacial acetic acid, instead of regenerating the ketone, completely disrupts a small proportion of the ngaiol, leaving the remainder intact.

All attempts to obtain a crystalline derivative of ngaiol have been unsuccessful (compare farnesol, which gives no crystalline derivatives). The acid phthalate and its *p*-nitrobenzyl ester (Reid, *J. Amer. Chem. Soc.*, 1917, **34**, 1249) are viscous syrups, and the phenyl- and α-naphthyl-urethanes are non-crystalline. The *methyl xanthate* (Tschugaev, *Ber.*, 1899, **32**, 213, 3332, etc.), purified from volatile products by steam distillation, is a mobile, light-yellow liquid (Found: S, 19·2. $C_{17}H_{26}O_3S_2$ requires S, 18·7%).

Ngaiol acetate, which is easily prepared in the usual way with acetic anhydride and sodium acetate, is a yellow oil, b. p. 190—192°/29 mm., $d_{20^\circ}^{20^\circ}$ 1·0337, $n_D^{20^\circ}$ 1·4720, $[R_L]_D$ 79·60. $C_{15}H_{23}O_2{\cdot}O{\cdot}CO{\cdot}CH_3$, $\overline{2}$, requires 80·31. Saponification value, 192. Theory for monoacetate, 185. The acetate decomposes slightly on distillation and for this reason always contains a small amount of free acetic acid. Heating with acetic anhydride in a sealed tube at 170—180° for 8 hours caused much resinification, but a small amount of oil was isolated, the saponification value of which was 204. Analysis showed that no water had been removed. By saponification with alcoholic potash and distillation in steam, ngaiol can be recovered from the acetate with unchanged physical constants.

The remaining two oxygen atoms are not attacked by acetic anhydride in presence of a drop of sulphuric acid at 0°. In order

as far as possible to avoid any hydrolysis of a sensitive ester group the product was isolated by distillation, after removal of sulphuric acid with calcium carbonate and decomposition of the excess of acetic anhydride by digestion with absolute alcohol. The saponification value of the product was 186.

Ngaiol benzoate cannot be prepared by the Schotten–Baumann method. By the pyridine method it is obtained as an oil which decomposes on distillation (compare daucol, *loc. cit.*). A quantitative experiment with benzoic anhydride according to Gascard (*J. Pharm. Chim.*, 1906, **24**, 97) showed that only one hydroxyl group was esterified. Ngaiol does not form a *p*-nitrobenzoate either by the Schotten–Baumann or the pyridine method.

Ngaiol monomethyl ether is a light yellow, almost inodorous oil. Three grams of potassium (2 mols.) were dissolved in 8 g. of pure tertiary amyl alcohol and 50 c.c. of dry toluene, and 10 g. of ngaiol were added to the hot solution. The mixture was cooled in running water while being gradually treated during 2 hours with excess (12 g.) of methyl iodide. After 12 hours, the mixture was warmed on the water-bath till neutral ($\frac{1}{2}$ hour), treated with water, and the toluene layer dried and distilled: b. p. 178—179°/29 mm. (182° corr.), $d_{20^\circ}^{20^\circ}$ 0·9913, $[\alpha]_D$ −16·82°, $n_D^{20^\circ}$ 1·4701, $[R_L]_D$ 74·89. Calculated for $\equiv_2$, 75·68 (Found: OMe, 11·1. $C_{15}H_{23}O_2{\cdot}OMe$ requires OMe, 11·6%). In the Zeisel determination ngaiol is converted into a resinous substance which dissolves completely in organic solvents. No deposit of carbon was formed, showing that a methylenedioxy-group is not present in the molecule.

Ngaiol methyl ether (3·30 g.) in dry boiling toluene dissolved one atom. of potassium in 6 hours and a second atom. in another 20 hours. The solution of potassium salt reacted slowly with methyl iodide in the cold. After 12 hours, the mixture was heated on the water-bath till neutral, and worked up in the usual way (Found for distilled product: OMe, 11·8%). It is noteworthy that calameone (*loc. cit.*) is regenerated unchanged when methyl iodide is allowed to act on its sodium salt.

The above experiments show that ngaiol contains probably only one hydroxyl group, and therefore that ngaione and ngaiol contain two internal ether groupings.

The work is being continued.

Part of this research was carried out at Otago University, Dunedin, New Zealand, while the author was holder of the John Edmond Research Fellowship. The still used in the extraction of the oil was obtained by aid of a grant from the New Zealand Institute. The author desires to express his thanks to the New Zealand

Institute and to the Chemical Society for research grants, and to Professor Inglis, Professor Collie, and Dr. Brady for their interest in the work.

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UNIVERSITY COLLEGE, LONDON. [*Received, June 11th*, 1925.]

CCXCIX.—*An X-Ray Examination of Maleic and Fumaric Acids.*

By KATHLEEN YARDLEY.

THE following investigation was undertaken primarily to determine whether the planosymmetry and centrosymmetry usually ascribed to maleic and fumaric acids respectively have any actual existence in the crystalline state. Maleic acid crystallises in the monoclinic system, and fumaric acid (as will be shown later) in the triclinic.

The crystallographic data for maleic acid ($M = 116$) are given by Groth ("Chemische Krystallographie," Part III, p. 286) as follows: Density $\rho = 1{\cdot}590$ g./c.c.; m. p. 130°; monoclinic prismatic, $a : b : c = 0{\cdot}7386 : 1 : 0{\cdot}7015$, $\beta = 117°7'$.

A preliminary investigation showed that the full (010) spacing was 10·11 Å.U. and substitution in the usual formula, $abc \sin\beta \,.\, \rho = 1{\cdot}65\, nM$, gives $n = 3{\cdot}96$ (4 mols./unit cell).

The spacings calculated on the basis $n = 4$ compare with the observed values as follows:

Plane (*hkl*).	Spacings calc.	Spacings obs.	Relative intensity of reflection.	Plane (*hkl*).	Spacings calc.	Spacings obs.	Relative intensity of reflection.
*100	6·67	3·31	Large.	310	2·17	2·16	Very small.
*010	10·14	5·05$_5$	Very large.	210	3·18	3·17	Small.
*001	6·33	3·16	Very large indeed.	320	2·03	2·03	Moderate.
				110	5·57	5·56	Large IInd order only.
041	2·35	2·35	Mod. large.				
021	3·96	3·92	Moderate.	230	2·37	2·36	Very large.
023	1·95	1·92	Very small.	120	4·04	4·04	Mod. small.
301	1·85	1·85	Mod. small.	130	3·02	3·01	Mod. large.
30$\bar{1}$	2·51	2·48	Mod. large.	140	2·37	2·35	Small.
*20$\bar{1}$	3·74	1·85	Moderate.	160	1·63	1·63	Small.
*30$\bar{2}$	2·41	1·19	Very small.	180	1·24	1·25	Small.
101	3·81	3·76	Moderate IInd order only.	11$\bar{3}$	2·28	2·27	Small.
				111	3·57	3·57	Moderate.
10$\bar{1}$	6·22	6·22	Mod. large IInd order only.	11$\bar{1}$	5·30	5·30	Mod. large.
				22$\bar{1}$	2·96	3·02	Small.
*10$\bar{2}$	3·56	1·77	Small.	12$\bar{1}$	3·93	3·93	Mod. large.
410	1·64	1·64	Small.	13$\bar{1}$	2·97	2·95	Small.

The crystals show a perfect cleavage parallel to the (001) plane, and twin on (100) so frequently that a single crystal could not at first be obtained and the spectrometer measurements were made

on a twin. This gave rather complicated results, but it was generally possible to detect which additional reflections were the result of the twinning. For example, since the crystal is monoclinic and twins on (100), the $\{hkO\}$ zone is entirely unaffected and the reflections found are perfectly normal. The $\{hOl\}$ zone, however, shows doubling of its planes throughout. Fig. 1 represents the lattice of the twin (showing four unit cells) projected on the (010) plane.

The reflections from the (101), (001), (10$\bar{2}$), (10$\bar{1}$), (20$\bar{1}$), etc., planes of one individual (A) of the twin are apparently doubled owing to reflections from planes (20$\bar{1}$), (10$\bar{1}$), (10$\bar{2}$), (001), (101), etc., belonging to the other individual (B). The (100) plane shows, of course, a single reflection, since it is common to both individuals; the angular separation is greatest between the (10$\bar{2}$)A plane and the (10$\bar{2}$)B plane. Measurement of the angle (001)A : (001)B gave for the monoclinic angle, $\beta = 117°10'$.

FIG. 1.

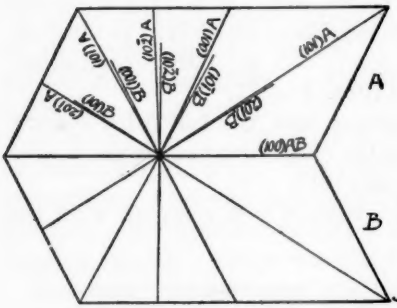
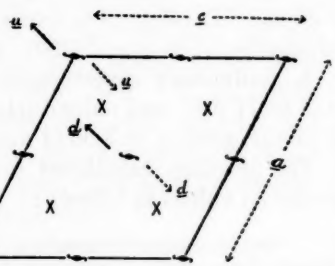


FIG. 2.



The reflections from planes of the $\{Okl\}$A zone may be confused with those from planes of the $\{hk\bar{h}\}$B zone, since the two zone axes are nearly parallel, and if one is vertical the other will be approximately vertical also. To eliminate all possibility of confusion of this kind, the measurements were repeated on a single crystal, grown from acetone after many attempts; several other planes also were measured. It was found, moreover, that, besides the perfect cleavage parallel to (001), there was an imperfect cleavage parallel to (010), and also that the crystals could be bent and twisted in certain directions without fracture. This interesting fact was verified both on single and on twinned crystals and will be described more fully in a separate paper.

The table of results shows that certain planes (marked *) have an observed spacing of only one-half of the calculated value. In other words, all odd-order reflections were absent from these planes. Apart from the (010) plane, all the marked planes have indices

$\{h0l\}$, where $(h + l)$ is odd. Since full spacings were found for the (301) (30$\bar{1}$) planes, the (101) (10$\bar{1}$) cannot really be halved, although only second-order reflections were found from these planes. The second-order reflection from the (010) plane was very strong, and moreover the planes for which k is odd gave much weaker reflections than those for which k is even. Thus the reflections from (011) and (031) could not be found, but those from (021) and (041) were quite strong; also the (160) and (180) reflections were easily measurable, whereas the (150) and (170) were not. The crystals therefore belong to the space-group C_{2h}^5, for which the (010) plane is halved and also all planes $\{h0l\}$ for which $(h + l)$ is odd (Astbury and Yardley, *Phil. Trans.*, 1924, *A*, **224**, 221). Rotation photographs, kindly taken by Dr. Müller, verified the spectrometer readings and the above conclusions. A diagrammatic representation of the space-group is shown in Fig. 2, in which the unit cell is projected on the glide-plane of symmetry, (010), and the positions of the centres of symmetry are marked by crosses.

Since there are four molecules in the unit cell, the maleic acid molecule must be asymmetric. The planosymmetry usually ascribed to maleic acid from chemical considerations has therefore no existence in the crystalline state. (It is, of course, possible that in solution the molecules do possess a plane of symmetry which is destroyed by slight distortion in the process of crystallisation). The absence of a plane of symmetry is perhaps surprising, as maleic acid on oxidation forms the internally compensated *meso*tartaric acid. It is, however, significant that, although maleic and succinic anhydrides are supposed to be isomorphous, the acids themselves are certainly not. Succinic acid belongs to the space-group C_{2h}^2 with two molecules per unit cell, and the molecule does, presumably, possess a plane of symmetry (Yardley, *Proc. Roy. Soc.*, 1924, *A*, **105**, 451), but its crystals are quite unlike those of maleic acid except in that they belong to the same class. The co-ordinates of equivalent points of the four molecules of maleic acid in the unit cell, relative to the crystallographic axes, are (000), $(\frac{1}{2}v\frac{1}{2})$, $(u\frac{1}{2}w)$, $(u + \frac{1}{2}, v + \frac{1}{2}, w + \frac{1}{2})$. Exact consideration of the relative intensities of reflection from different planes is not likely to be very helpful in deciding the values of the variable parameters, u, v, w, as the positions of the atoms in the molecule are not known. There are, however, some general indications of their value. For instance, since very large second-order but no first-order reflections were found for the (101) (10$\bar{1}$) planes, it seems probable that u and w are approximately equal to $\frac{1}{2}$ and 0 or 0 and $\frac{1}{2}$. Also the exceptionally large reflection from the (001) planes, parallel to which is an excellent cleavage, indicates that most of the atoms lie in these planes and

very few between them. The following structure is suggested as being most probably near to the truth, though not by any means as being correct in every detail. In general, the actual measurements completely define the lattice and space-group, but the

FIG. 3.

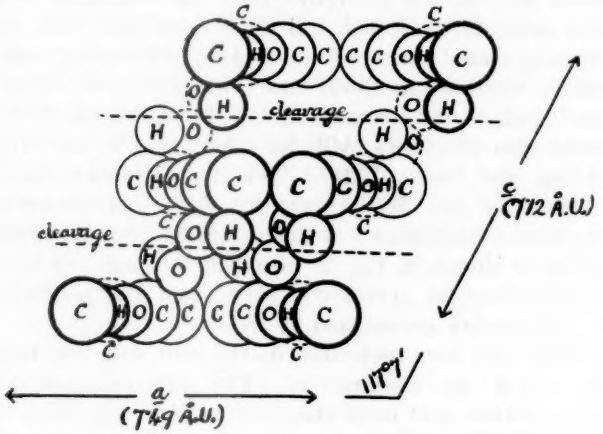
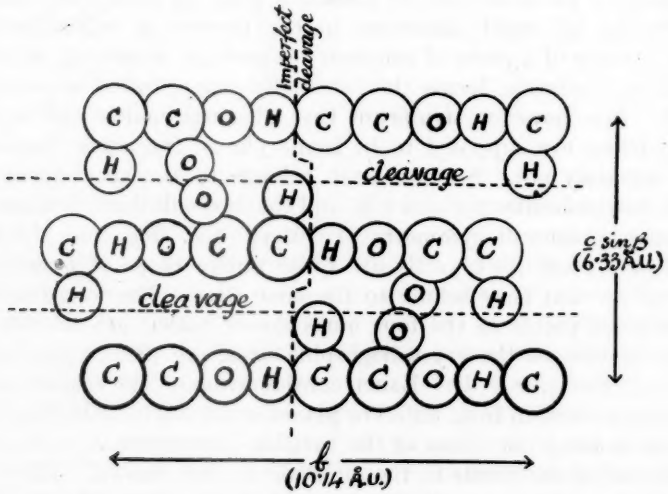


FIG. 4.

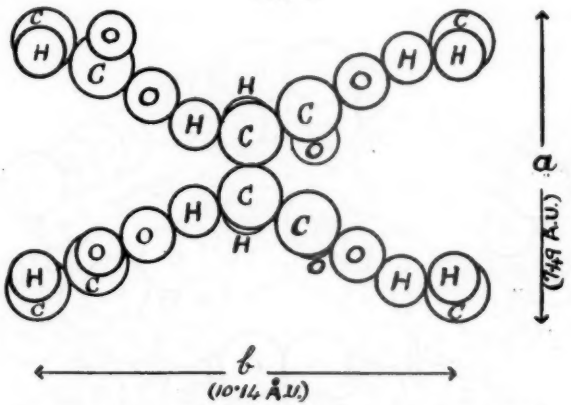


assignment of a structure, however probable or plausible, is always accompanied by a certain amount of conjecture. The suggested structure for maleic acid is based on the known space-group C_{2h}^5 and therefore on the simple Bravais lattice Γ_m. In order to explain the very large reflection from the cleavage plane (001) it is necessary

to assume that the double bond lies along the a axis and the two C–C–OH groups lie wholly in the (001) plane, linking between the (001) planes being effected by means of the ketonic oxygen atoms only. Since it is not probable that two ketonic oxygen atoms will attract each other with any great force (indeed, repulsion is more likely), the cleavage parallel to the (001) planes is readily explained. This is illustrated diagrammatically in Figs. 3 and 4.

In Fig. 3 is shown the projection of the unit cell on the (010) plane of symmetry. The measurements show that the molecule at the point $(\frac{1}{2}, v, \frac{1}{2})$ is the reflection of that at the origin. The only satisfactory way of placing the remaining two molecules is for the molecule which is obtained by rotation of that at the origin to lie at

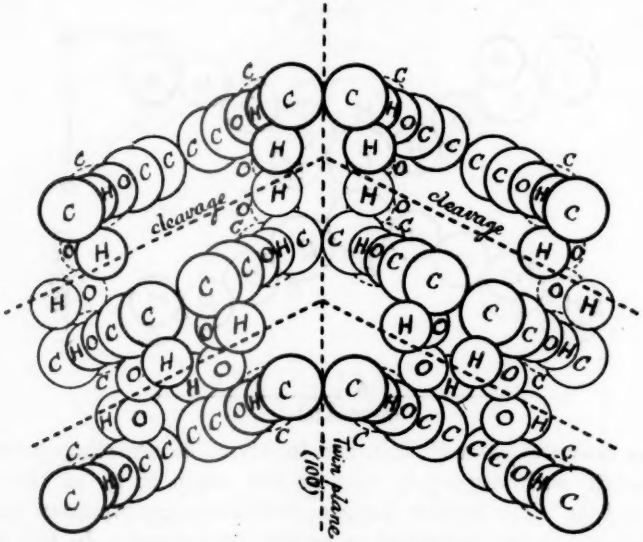
FIG. 5.



or very near the point $(\frac{1}{2}, \frac{1}{2}, 0)$ and for the molecule which is centrosymmetric with respect to that at the origin to lie at the point $(0, v + \frac{1}{2}, \frac{1}{2})$. The ketonic oxygen atoms lie approximately parallel to the c axis when projected on to the (010) plane. In Fig. 4, the projection is on a plane normal to the a axis. Here both cleavages are clearly seen, and it will also be noticed that the hydrogen of the carboxyl group of one molecule links on to the unsaturated carbon of the next. The exact positions of the hydrogen atoms cannot, of course, be fixed, since their scattering power is too small seriously to affect the X-ray reflections. In Fig. 5, which shows just the atoms lying in the (001) plane and those directly connected to them, the asymmetry of the molecule is at once apparent, and a comparison of the various diagrams shows that such asymmetry is necessary to build up the monoclinic structure. It is essential that such a structure should explain the almost invariable twinning on the (100) plane. Multiple twinning never appeared at all; in fact, examination of the crystals at various stages of their growth tended

to prove that a crystal began to grow at the twin plane and then built itself up to equal amounts on either side of this. The material crystallised at first in long, fine needles, which afterwards increased in thickness. However fine these needles might be, they were always perfect twins, and the smaller the crystal the more nearly exactly was it bisected parallel to its length by the twin plane. If these needles were broken across, a remarkably good re-entrant cleavage was observed, parallel to the (001) plane in each individual of the twin. In the case of a cluster of needle-like twins growing out from a complex nucleus, the apex of the re-entrant angle cleavage always pointed towards the nucleus, showing that the crystal growth

FIG. 6.

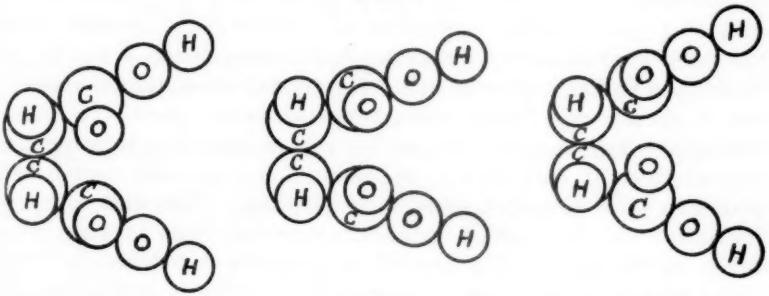


had followed certain clearly defined lines in the case of each needle. When crystallisation had taken place fairly rapidly, none of the crystals were single, although by slowing down the rate of evaporation it was sometimes possible to obtain large crystals which had grown unevenly on either side of the twin plane. From these one or two single individuals could be detached. Now if we assume that the crystals start growing as single individuals and then suddenly change direction and form twins, it is not easy to explain either the absence of multiple twinning or the presence of twinning in the very smallest crystals. These facts are readily explained on the hypothesis that growth begins at the twin plane. In that case, since the twin plane is a plane of reflection, molecules lying in it would necessarily possess a plane of symmetry, and would

therefore be slightly different from those in the main body of the crystal. This is not improbable, as a little consideration will show. The molecules in the suggested structure are distorted but very little out of their symmetrical form; in solution, these molecules probably do possess a plane of symmetry (or other two-fold symmetry), since there is no reason from a chemical point of view why one-half of the molecule should differ from the other. When, therefore, crystallisation first begins, it is probable that the molecules will form themselves into a sheet, retaining their original symmetry. On either side of this sheet the crystal would build itself up as shown in Fig. 6.

The molecules on either side of the central twin plane would be pulled out by the next succeeding layer and thus would become asymmetric, but the molecules lying *in* the twin plane, being pulled

FIG. 7.



equally on either side, would not lose their plane of symmetry. The re-entrant cleavage is also easily explained. It is to be expected that at the twin plane the structure would be somewhat strained; in fact, the two individuals can be separated at the twin plane, though there is no cleavage parallel to the (100) plane in any other part of the crystal. An asymmetric molecule and its reflection are non-superposable and so, unless it is assumed that the asymmetry is merely distortion produced during the process of crystallisation, it is impossible to avoid the conclusion that the original solution contained two enantiomorphous kinds of molecules. This is most unlikely.

In Fig. 7, (*b*) represents the undistorted molecule with its plane of symmetry, as it would occur at the twin plane; (*a*) and (*c*) show the molecule distorted in opposite directions, thus accounting for the asymmetric enantiomorphous forms. The approximate atomic diameters in this structure are: C = 1·54 Å.U., O: = 1·15, OH = 2·5, H = 1·15. It is not possible to tell whether the atomic diameter

of the unsaturated carbon atom differs from that of the saturated, especially as in the suggested structure both carbon atoms are, in effect, saturated.

The measurement of crystals of fumaric acid was much more difficult than that of maleic acid. No previous crystallographic data were available, as the crystals grown are utterly unsuited to the usual goniometric examination. They are small and copiously twinned in many directions, and most crystals show either no clear face at all or only one. Nearly all of the fumaric derivatives that have been measured belong to the triclinic system, and it seemed probable that that would prove to be the case for the acid also. Fortunately, by slow evaporation of an aqueous solution, one crystal was obtained that seemed to be twinned in one direction only. Measurements were made on this crystal, the Bragg ionisation spectrometer being used (as before) together with a Coolidge tube of rhodium anticathode. The main planes were first localised by obtaining the "mirror" reflection of "white" X-radiation, and the position of the actual reflection of the homogeneous X-ray beam could then be found quite easily. The crystal was almost shapeless, but it showed one bright, though by no means plane, face. By setting this face as nearly as possible vertical and then rotating the crystal about it very slowly, the main zone axes were found and planes in three principal zones were measured. The unit cell was triclinic. The face which actually grows on some crystals was taken as the (001). The crystal measured was twinned on this plane, which was also a good cleavage plane. Nearly at right angles to it was a second, less definite, cleavage plane which was taken as the (010). A third plane nearly normal to these two was taken as the (100). These planes having been arbitrarily selected as axial planes, the spacings of other planes in the axial zones were measured. By combining all the observations it was possible to determine the size of the minimum crystallographic cell. The unit cell taken is, of course, in the triclinic system, only one of an infinite number of minimum cells all having the same volume. The conditions that any such unit cell must fulfil are (1) that no calculated spacing should be a sub-multiple of the corresponding measured spacing, and (2) that no set of calculated spacings should be multiples of the measured spacings of those planes. If, for example, the measured spacing of each plane with indices $\{hkl\}$, where h is odd, were one-half of the calculated value, it would mean that the unit cell adopted was twice as large as the true unit cell, the a axis of the latter being only one-half the length of the a axis formerly used.

Considerations such as these showed that the arbitrarily selected axial planes did form the boundaries of one such possible minimum

cell. The angles between the axial planes and their spacings were measured; the lengths of the axes and the axial angles calculated therefrom are $a = 7{\cdot}56$, $b = 15{\cdot}00$, $c = 6{\cdot}20$ Å.U., whence $a : b : c = 0{\cdot}504 : 1 : 0{\cdot}413$ and $\alpha = 90°40'$, $\beta = 88°30'$, and $\gamma = 89°48'$.

As these angles are all very nearly right angles, they are almost exact supplements of the measured angles between the axial planes. Also the differences between the lengths of the axes a, b, c, and the observed spacings d_{100}, d_{010}, d_{001} are less than the probable errors of observation and are therefore negligible. From these axial spacings and angles the spacing, d, of any other plane (hkl) can be calculated by means of the formula

$$\frac{N^2}{d^2} = \frac{h^2}{a^2}\sin^2\alpha + \frac{k^2}{b^2}\sin^2\beta + \frac{l^2}{c^2}\sin^2\gamma + 2\left[\frac{kl}{bc}(\cos\beta\cos\gamma - \cos\alpha) + \frac{lh}{ca}(\cos\gamma\cos\alpha - \cos\beta) + \frac{hk}{ab}(\cos\alpha\cos\beta - \cos\gamma)\right]$$
$$= \sum\frac{h_2}{a_2}\sin^2\alpha + 2\sum\frac{kl}{bc}(\cos\beta\cos\gamma - \cos\alpha),$$

where $N^2 = 1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma$
$= 4\sin\tfrac{1}{2}(\alpha+\beta+\gamma)\sin\tfrac{1}{2}(-\alpha+\beta+\gamma)\sin\tfrac{1}{2}(\alpha-\beta+\gamma)\sin\tfrac{1}{2}(\alpha+\beta-\gamma)$.

Also the angle θ between two planes $(h_1k_1l_1)$ and $(h_2k_2l_2)$ is given by

$$\cos\theta = \frac{d_1d_2}{N^4}\left[\frac{h_1h_2}{a^2}\sin^2\alpha + \frac{k_1k_2}{b^2}\sin^2\beta + \frac{l_1l_2}{c^2}\sin^2\gamma + \frac{h_1k_2 + h_2k_1}{ab}(\cos\alpha\cos\beta - \cos\gamma) + \frac{k_1l_2 + k_2l_1}{bc}(\cos\beta\cos\gamma - \cos\alpha) + \frac{l_1h_2 + l_2h_1}{ca}\cos\gamma\cos\alpha - \cos\beta)\right]$$
$$= \frac{d_1d_2}{N^4}\left[\sum\frac{h_1h_2}{a^2}\sin^2\alpha + \sum\frac{k_1l_2}{bc}(\cos\beta\cos\gamma - \cos\alpha)\right],$$

d_1, d_2 being the spacings of the two planes.

The volume of the unit cell is $abcN$.

Comparison can thus be made between the spacings and angles calculated as above and those actually measured on the spectrometer.

Spacings.

Plane.	Calc.	Obs.	Relative intensity.	Plane.	Calc.	Obs.	Relative intensity.
100	—	7·56	Small II.	$30\bar{1}$	2·36	2·36	Mod. large.
010	—	15·00	Moderate VI.	101	4·73	4·74	Very small I, small III.
001	—	6·20	Small I, very large II.	$10\bar{1}$	4·86	4·83	Very small I, small III.
012	3·04	3·04	Mod. large.				
$01\bar{2}$	3·03	$3{\cdot}03_5$	Mod. large.	110	6·74	6·70	Mod. small II, III.
031	3·91	$3{\cdot}89_5$	Moderate.	$1\bar{1}0$	6·76	6·75	Mod. small II, III.
$03\bar{1}$	3·87	$3{\cdot}88_5$	Moderate.	210	3·66	3·59	Moderate.
041	3·23	—	Not found.	$2\bar{1}0$	3·67	$3{\cdot}60_5$	Mod. large.
$04\bar{1}$	3·19	3·20	Small.	140	3·36	3·35	Small.
301	2·31	2·32	Mod. large.	$14\bar{0}$	3·37	3·37	Small.

Angles between planes.

Planes.	Calc.	Obs.	Planes.	Calc.	Obs.
010 : 001	—	89° 20′	$30\bar{1}$: 001	69° 10′	68° 51′
001 : 100	—	91 30	$10\bar{1}$: 001	141 17	141 20
100 : 010	—	90 12	$10\bar{1}$: 001	39 56	39 36
012 : 001	168° 24′	168 12	$1\bar{1}0$: 010	116 57	116 40
$01\bar{2}$: 001	11 35	11 37	$1\bar{1}0$: 010	63 25	63 17
031 : 001	128 31	128 32	$2\bar{1}0$: 010	104 19	104 18
$03\bar{1}$: 001	50 42	50 43	$2\bar{1}0$: 010	76 3	76 8
041 : 001	58 21	58 32	$1\bar{4}0$: 010	153 31	153 36
301 : 001	113 25	113 28	$1\bar{4}0$: 010	26 34	26 50

Allowance being made for the obvious difficulties in setting the crystal on the spectrometer table in the correct position, this agreement is quite good.

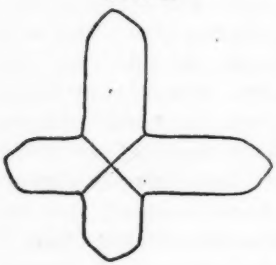
The density of fumaric acid is 1·625 g./c.c. and $M = 116$. Calling the number of molecules per unit cell n, we have $abcN\rho = nM.1{\cdot}65$. Substitution of the known values of a, b, c and N leads to the value $n = 5{\cdot}97$.

This shows that there are six molecules of formula $C_2H_2(CO_2H)_2$ in the unit cell, the *minimum* cell which, repeated through space, will build up the crystal structure. It is well-known, however, that the number of asymmetric units required to build up a triclinic cell is either one or two. A triclinic pedial (C_1) crystal is formed by the repetition through space of a single asymmetric unit, a triclinic pinakoidal (C_i) crystal by the repetition through space of one centrosymmetric unit or of two asymmetric units arranged centrosymmetrically with respect to each other. Now it is impossible from the outward form of the fumaric acid crystals to tell whether they belong to the pedial or to the pinakoidal class, since all the crystals are practically shapeless, nor is it possible by any X-ray method to distinguish between the two classes. If the crystals belong to the pedial class, then it follows that six simple molecules of formula $C_2H_2(CO_2H)_2$ must, in the solid state, be associated together to form a single asymmetric unit, which is then repeated through space. If, on the other hand, the crystals are pinakoidal, then the six molecules in the unit cell are arranged in two groups of three, each group being asymmetric in itself, but centrosymmetric with respect to the other. It is important to know whether the simple chemical molecules in such a group are related to one another in a manner different from that in which they are related to all other molecules in the crystal. If this is so, then the group might be called a "crystal molecule," its formula being $[C_2H_2(CO_2H)_2]_6$ in the first case or $[C_2H_2(CO_2H)_2]_3$ in the second. In the unit cell of any symmetrical crystal there exists an association of a given number of ultimate asymmetric parts which are so arranged about the elements of symmetry as to build

up a unit possessing the full symmetry of the class. This unit then repeats itself through space without change of character or orientation. In general, the ultimate asymmetric parts are identical with the chemical molecule (or ions) or are sub-multiples of the chemical molecule. Thus, in the case of naphthalene the molecule is centrosymmetric (that is, it contains two such parts) and two molecules arranged about an axis of screw symmetry build up the unit monoclinic prismatic cell. There is certainly no reason why one should pair a given molecule in such a crystal with any of its four immediate neighbours and call such a pair a double molecule. The case of fumaric acid is, however, quite different. This is one of the few exceptional crystals where the ultimate asymmetric part is a multiple of the simple chemical molecule. Other examples which have been found include α-naphthylamine (Sir W. H. Bragg, Report of the Solway Conference, 1925), where the orthorhombic cell contains eight asymmetric groups of three chemical molecules; monoclinic carbon tetrabromide (Mark, *Ber.*, 1924, **57**, 1820), where the ultimate part is said to be C_2Br_8; and rhombic sulphur (Mark and Wigner, *Z. physikal. Chem.*, 1924, **111**, 398), in which the unit cell contains 128 atoms, the ultimate asymmetric group being either S_4, S_8, or S_{16}. As a rule, when two or more chemical molecules are associated together in the unit cell it is with the object of producing symmetry. When, as in these exceptional cases, there is also an association of a type which does not produce symmetry, we are perhaps justified in assuming that this association is closer than a mere crystallographic connexion and partakes more of the nature of an actual polymerisation in the solid state. In the case of sulphur it is most probable that the different crystalline forms are polymerised to different extents; the polymerisation is known to persist to a certain extent even in the vapour. This point has not been tested in the case of fumaric acid. Very little is known about matter in the solid state, apart from what can be directly deduced from the crystal structure. The fact that fumaric acid sublimes at 200° and melts in a closed tube only at 286—287° may perhaps be taken as evidence of a closer association between the chemical molecules than that usually existing in crystals. The same possibly applies to its insolubility in all ordinary solvents, and to its low heat of combustion (317·6 mol.-gm.-cals.) compared with that of maleic acid (331·3 mol.-gm.-cals.), since it may well be supposed that in the case of fumaric acid heat would be used up in separating the molecules before actual combustion could take place. It is doubtful, however, whether any reliance can at present be placed on conclusions drawn from differences in heats of combustion, heats of solution or crystallisation, etc., since we have very little idea to

what extent these depend on the actual crystal structure and to what extent on the molecular structure (Garner and Randall, J., 1924, **125**, 881). Bruni and Gorni (*Gazzetta*, 1900, **30**, i, 80), when determining the molecular weights of methyl maleate and fumarate cryoscopically in methyl succinate, found a normal value for the maleic ester (149·5 to 164; calc., 144), but the abnormal value of 797 to 914 for the fumaric ester in dilute solution; a raising of the freezing point of more concentrated solutions (above 2%) probably indicated the formation of a solid solution of the fumaric with the succinic ester. The abnormal value obtained for the fumaric ester in dilute solution may possibly be due to molecular association of the same type as that now observed in the case of the acid. Deductions drawn from the behaviour of the esters could not, however, be safely applied to the acids. That there is some difference between maleic and fumaric acids other than this association is obvious, since in solution they both act as if they had the simple formula and yet there are striking chemical differences to be accounted for. Probably there is a difference in the spatial arrangements of the atoms in the simple molecules in solution, but in neither case does the molecule possess symmetry in the crystalline state.

FIG. 8.



The complex twinning mentioned above as characteristic of fumaric acid is worth describing in some detail. Cruciform growths are very frequent (as shown in Fig. 8). The only distinct face on such a twin is the flat surface, from which a small reflection has been obtained showing it to be the {001} plane. The twin planes therefore have indices {*hkO*}. The angles between the arms of the twin are almost exact right angles and the *b* axis runs parallel to the length of the arms. Hence the twin planes must be the {120} and {1$\bar{2}$0}, which make angles of 44°42′ and 44°55′ respectively with the {010} plane. Some crystals are twinned in the above manner and then again each arm is twinned on a plane nearly at right angles to both {001} and {010}, presumably therefore the {100}. Such interpenetrating twins obey at least two twin laws. Other interpenetrating twins have not merely four arms, but six. Some have only four arms, but these are not at right angles. The laws obeyed by such twins have not yet been elucidated.

More recent *X*-ray examination of some of the derivatives of maleic and fumaric acids has shown that in no other case yet investigated does association take place in the solid state. The substances examined were monopotassium chloromaleate, $C_4H_2O_4ClK$,

diammonium chlorofumarate, $C_4HO_4Cl(NH_4)_2$, and ammonium hydrogen fumarate, $C_4H_3O_4NH_4$; the *X*-ray data obtained have been published elsewhere (Yardley, *Phil. Mag.*, 1925, **50**, 864).

In conclusion, I wish to thank Professor Sir William H. Bragg, F.R.S., most heartily for his constant encouragement and advice. My grateful acknowledgments are also due to the Advisory Council of the Department of Scientific and Industrial Research and to the Royal Institution for rendering financial and laboratory assistance. For the preparation of the three compounds last mentioned, I am very much indebted to Mr. W. B. Saville.

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ROYAL INSTITUTION. [*Received, May 19th*, 1925.]

CCC.—*Purification of Phosphoric Oxide.**

By HENRY WHITAKER.

FINCH and PETO purified phosphoric oxide from traces of lower oxides by subliming it in a current of oxygen in an iron tube, heated to redness, and collecting the sublimate in a cooled glass tube (J., 1922, **121**, 692). On repeating the experiment, the chief difficulties encountered were the blocking of the glass tube with a solid crust of oxide and its frequent fracture at the glass-to-iron junction. Better results were obtained by employing a special form of receiver.

The receiver shown in Fig. 1 consists of a T-piece of wide glass tubing, the lower end, *b*, of which is fitted by means of a cork to the wide-necked bottle, *c*; transference of the sublimate from the receiver to a bottle for storage is thus avoided.

The receiver shown in Fig. 2 was made by sealing the wide tube, *b*, close to the end of a (broken) Liebig's condenser jacket, which was drawn out at *e* to fit into the end of the iron tube. The glass ram, *a*, served to rake down into the bottle any deposit which collected at *f*, and the tube *b* was kept clear by occasional raking with a glass rod, applied through *d*, which was normally closed with a cork. In the glass-to-iron junctions at *e*, a packing consisting of a collar of thin asbestos paper was found preferable to cementing with phosphoric acid. The chief drawback of either form of receiver, however, was fracture, which invariably occurred sooner or later in the course of the experiment. An iron T-piece was next tried, which proved more satisfactory.

* The work now described was completed in 1922. The peculiar difficulties attending the distillation of phosphoric oxide are disclosed by the work of Smits and Rutgers (J., 1924, **125**, 2573).

The bent glass tube, with rake, employed by Finch and Peto for admitting small quantities of phosphoric oxide at a time into the iron tube was found to be inconvenient, and a simple form of feeding apparatus was substituted, which proved entirely successful. It consists of a wide glass tube, drawn out and sealed to the end of a thinner glass tube and provided with an ordinary cork, through which passes a glass rod flattened at the end into a circular disk. The glass rod should slide easily through the cork and the circular disk should loosely fit the narrow tube. The dropping tube is charged by raising the cork, keeping the glass rod in position with

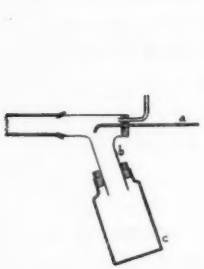

Fig 1

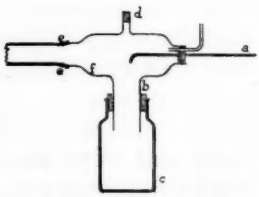

Fig 2

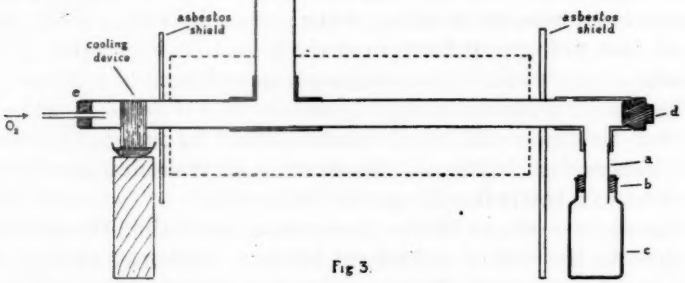

Fig 3.

the disk closing the narrow tube; the cork is then slid back into position. The crude phosphoric oxide contained in the dropping tube can be admitted as required, by slightly raising the glass rod and tapping the tube. This form of apparatus can be repeatedly recharged with fresh phosphoric oxide without interrupting the experiment.

Blockages tended to occur in the vertical limb of the central iron T-piece; these were eliminated by using a vertical tube of wider diameter than the horizontal portion. The final form of the apparatus is shown in Fig. 3.

The current of oxygen (dried by passage through sulphuric acid, stick caustic potash, and crude phosphoric oxide) enters the iron

tube at *e*. It was found unnecessary to have an exit tube for the escaping oxygen. By properly adjusting the "fit" of the bottle *c* (receiver for the sublimed phosphoric oxide) to the cork *b*, fitted over the iron tube, *a*, the oxygen escaped *viâ b*. During the progress of an experiment, the plug, *d*, is unscrewed occasionally and the iron T-piece raked with an iron rake.

In one experiment, from approximately 200 g. of impure phosphoric oxide, 70 g. of pure pentoxide were obtained in 2 hours. This product, tested with silver nitrate in the manner suggested by Finch and Peto, was found to be free from lower oxides.

The use of mercuric chloride as a reagent for detecting the presence of lower oxides of phosphorus (suggested by Sir Richard Threlfall in a private communication to Professor A. Smithells) was found to be more convenient than silver nitrate, as neutralisation of the phosphoric acid with sodium hydroxide is unnecessary. A small quantity of the phosphoric oxide to be tested, dissolved in water, is boiled with mercuric chloride solution; if traces of phosphorous acid are present, a white turbidity or precipitate of mercurous chloride appears. All the samples of phosphoric oxide prepared by the method described above, when thus tested, were found to be free from lower oxides.

THE UNIVERSITY, LEEDS. [*Received, August 20th*, 1925.]

CCCI.—*Determination of Metals Dissolved in Mercury. Rapid Method of Purifying Mercury.*

By ALEXANDER SMITH RUSSELL and DEREK CURTIS EVANS.

THE work to be described is dependent on two observations, both of which, we think, are new: (1) that all metals more electropositive than mercury except cobalt go rapidly into solution as sulphates without the accompaniment of mercury when amalgams of them are shaken with potassium permanganate or certain other oxidising agents in dilute sulphuric acid, and (2) that the point at which the last trace of the metal in the mercury has gone into solution is shown by the breaking of the surface of the mercury into bubbles. For the determination of single metals in mercury by the method to be described it is necessary that the reducing power of the metal be 100%, that is to say, that the metal go into solution only in so far as it reduces the permanganate or other oxidising solution. For purifying mercury, on the other hand, rapidity of action between the metals to be removed and the

oxidising solution is more necessary than efficiency of reducing power.

We find * that the order in which metals when dissolved in mercury are removed from it by oxidising solutions is not the same as that of the electrode potentials of the metals in the free state. This order in mercury is (proceeding from electropositive to noble metals and including only those with which we have experimented) : zinc, manganese, cadmium, thallium, tin, lead, copper, chromium and iron, bismuth, cobalt, mercury, and nickel. It was found by obtaining the metals two at a time in mercury and finding out which went first into solution when ferric sulphate, or potassium permanganate or uranyl sulphate in sulphuric acid was reduced. The order seems quite definite; it appears to be the same whatever oxidising solution be reduced, whether the solution be hot or cold, whether sulphuric or hydrochloric acid be employed, and whatever other metals be present in the amalgam. The order in mercury differs from the order of the electrode potentials of metals in the free state only in the absolute positions of chromium, manganese, iron, cobalt, and nickel (atomic numbers 24 to 28). This is ascribed to passivity (Russell, *loc. cit.*). The relative order of these elements in both series is the same.

Experimental.

The reducing efficiency of a metal in mercury was investigated as follows : an amalgam containing from 0·2 to 0·4 g. of the metal in 200 g. of mercury was prepared either by direct solution, or by electrolysing solutions of sulphate in sulphuric acid the concentrations of which before and after electrolysis had been determined; the amalgam was shaken in a 300 c.c. stoppered bottle with 80 c.c. of 2N-sulphuric acid and a volume of accurately N/10-potassium permanganate until the pink colour was just discharged; further volumes of permanganate were run into the bottle and the colour discharged until a point was reached such that on further shaking the surface of the mercury became a mass of small bubbles. This point could be accurately judged with experience to about 0·2 or 0·3 c.c. and was taken as the point at which the whole of the metal had left the mercury. The mass of the metal theoretically necessary to oxidise the volume of reduced permanganate was then compared with the known weight contained originally in the mercury.

* This experimental work with discussion will be published elsewhere. In *Nature*, 1925, **115**, 455, one of us (A. S. R.) gave this order slightly differently. By a slip *chromium* read *manganese*. The position of manganese had not then been investigated.

The results obtained for seven metals and potassium permanganate are in the table below.

Gram taken.	Gram found.	% efficiency.	Gram taken.	Gram found.	% efficiency.
	Zinc.			Lead.	
0·210	0·193	91·9	0·100	0·101	101
0·210	0·192	91·4	0·202	0·200	99
0·219	0·200	91·3	0·205	0·206	100·5
0·929	0·865	93·1	0·206	0·206	100
			0·406	0·410	101
	Cadmium.			Copper.	
0·222	0·222	100	0·1115	0·1115	100
0·230	0·228	99·1	0·1673	0·1680	100·4
0·263	0·261	99·2		Iron.	
0·281	0·279	99·3	0·1791	0·1722	96·1
	Tin.		0·3658	0·3515	96·1
0·400	0·400	100		Bismuth.	
0·401	0·402	100·2	0·302	0·302	100
0·403	0·400	99·2	0·367	0·365	99·5
0·403	0·401	99·5			

It is seen that the results obtained by this rapid method (an experiment could be easily completed in 5 minutes) are fairly consistent and that each metal tried, with the exception of zinc and iron, is 100% efficient as oxidiser of potassium permanganate. These results contrast remarkably with the reducing efficiencies, and also the rate of oxidation, of some of these metals in the free state as investigated by Thorpe (J., 1882, **41**, 287) and Sugden (J., 1921, **119**, 233).

The results obtained in a similar manner when the metals reduced a $N/10$-solution of ferric sulphate in $2N$-sulphuric acid were approximately 100% for cadmium, tin, lead, copper, and bismuth, as with permanganate. Zinc, however, was now also 100% efficient, the actual values obtained being 100, 100·9, and 100·1. The reducing efficiency of iron was, however, again less than 100%, the values obtained varying from 94 to 97. Ferric sulphate was found to oxidise the metal of the amalgam much more rapidly than permanganate, and shaking had to be carefully done to avoid over-running the end-point and bringing some of the mercury itself into solution.

When uranyl sulphate was reduced, none of the metals showed reducing efficiencies of 100%. Of the seven metals mentioned above, only zinc, cadmium, tin, and lead could be investigated, because these alone were found to reduce uranium quantitatively from the sexavalent to the quadrivalent form. The mean values of their efficiencies decreased in decreasing order of potential, the mean values found being 91, 88, 82, and 74 for zinc, cadmium, tin, and lead, respectively.

It is obvious that the reducing efficiency of a metal may be investigated in this way only when it is completely removed from the mercury without being accompanied by mercury. It was found that mercury invariably accompanied cobalt and nickel when amalgams of these elements were shaken with oxidising solutions. The number of atoms of cobalt oxidised by the permanganate was found to be greater than that of mercury, and the number of atoms of nickel less. Cobalt appears, therefore, to act like a more electropositive and nickel like a more electronegative metal than mercury. It was found possible by sacrificing some mercury to remove the whole of the cobalt, but not the whole of the nickel from the mercury by shaking with oxidising solutions. These are the only metals which lie in potential between zinc and mercury in the free state which cannot be determined quantitatively by the method described in this paper.

The whole of these results receive a ready explanation with the help of present knowledge of the phenomenon of over-voltage. When a metal dissolved in, and more reactive than, mercury is shaken with sulphuric acid, it goes to some extent into solution and the equivalent amount of ionic hydrogen is discharged at the surface of the mercury. This has been proved to occur whether or not the metal is more electropositive than hydrogen in the potential series (S. W. J. Smith, *Phil. Mag.*, 1909, **17**, 834). Two extreme courses are open to this atomic hydrogen : it may wholly combine with the oxidising solution present (in which case the reducing efficiency of the metal is 100%), or it may wholly combine to form molecular hydrogen at the surface of the metal. The former course, it is expected, would be favoured by the presence of ions which are quickly reduced, and by a metal the power of which for catalysing the formation of molecular from atomic hydrogen is small; the latter course would be favoured by the presence of ions that are reduced slowly, and by a metal which catalyses the formation of molecular hydrogen. Of the three solutions tried, ferric sulphate was found by a series of comparative tests to be reduced most quickly, and uranyl sulphate most slowly, by amalgams of each of the metals investigated. Of these metals, mercury has the highest, and iron the lowest, hydrogen over-voltage, and, if this phenomenon be interpreted as the inability of the metal to catalyse the reaction $2H \longrightarrow H_2$, it follows that, of the metals under discussion, mercury does this most slowly and iron most quickly.

The experiments described above may now be explained. When potassium permanganate is reduced in acid solution, only the very reactive zinc can generate more hydrogen (or more reactive hydrogen) than can be retained at the surface of the metal until it

reacts with the permanganate. When ferric sulphate is reduced, the increased rate of reaction between it and the atomic hydrogen is sufficient to prevent any formation of molecular hydrogen; zinc is consequently, like the other metals, 100% efficient as a reducer. When uranyl sulphate is reduced, the slower rate of reaction between it and atomic hydrogen explains the smaller reducing efficiency of zinc. Comparative tests which we have made on the rate of reduction of uranyl sulphate in acid solution by amalgams of different metals, show that as the metal becomes more and more electronegative the rate at which it reduces uranyl sulphate relative to that at which it reduces permanganate decreases rapidly. Zinc, for example, reduces permanganate about 20% more rapidly than the less reactive lead under similar conditions; it reduces uranyl sulphate, however, about ten times more rapidly. These observations explain the low efficiencies of metals and their decrease with decrease in electrode potential when they reduce uranyl sulphate.

Since iron falls in the potential series of metals in mercury between copper and bismuth, it is to be expected from the results above that it would show a 100% reducing efficiency both with potassium permanganate and with ferric sulphate. The lower values found cannot be explained by supposing that the iron, which appears to be in the passive state in mercury, has become active, because there is no other evidence that iron when reducing permanganate or ferric sulphate becomes active, and further, zinc, which is 100% efficient as a reducer of ferric sulphate, is more electropositive than active iron. The explanation of the low values is that iron is the only metal in the amalgams investigated which so catalyses the reaction $2H \longrightarrow H_2$ that not all of the atomic hydrogen is used in reducing the oxidising solution. This is confirmed by the results of experiments on the reducing efficiency of zinc on permanganate in amalgams containing one other metal.

We find that cadmium, tin, and lead do not lower the reducing efficiency of zinc, that iron lowers it a little, and that tungsten, molybdenum, and platinum, which have very small hydrogen over-voltages, reduce it considerably. These experiments will be detailed in a separate communication. The following experiments lead more simply to the same result: (1) When a c.c. of $N/10$-permanganate are shaken in sulphuric acid solution with iron amalgam the permanganate is first reduced and the resulting ferric sulphate is then quantitatively reduced by more iron to the ferrous condition. When this solution is titrated with the same permanganate, it requires theoretically $a/2$ c.c., if iron has a reducing efficiency of 100%. Experimentally it requires usually from 0·2 to 0·5 c.c. in excess of this amount, showing that some of the iron

present in the amalgam has gone into solution without performing any reduction of either the permanganate or the ferric solutions present. (2) When a c.c. of $N/10$-ferric sulphate are shaken in sulphuric acid solution with iron amalgam a solution of ferrous sulphate results. This solution should theoretically require $3a/2$ c.c. of $N/10$-permanganate when titrated. Experimentally it requires from 0·2 to 0·5 c.c. in excess of this amount for the reason explained above. (3) When the same volume of the solution in (2) is shaken with a tin- instead of an iron-amalgam, ferrous sulphate and stannous sulphate but no stannic sulphate are found to form. This solution should theoretically require $2a$ c.c. of $N/10$-permanganate, since stannous sulphate and ferrous sulphate are formed in equivalent amounts. Experimentally this value is found, which shows that tin is 100% efficient in these circumstances.

From this survey it follows that, of the metals considered, iron alone cannot be directly determined in mercury by measuring the volume of potassium permanganate or ferric sulphate reduced by the metal. Owing to the rapidity of the reaction between the metal and the ferric sulphate and consequent danger of over-running the end-point, it is better to use potassium permanganate in presence of $2N$-sulphuric acid as oxidiser except when zinc is being determined. Iron may be determined easily and quantitatively by the following modification of the method. The iron amalgam is shaken with the permanganate until the end-point is obviously passed. The reduced solution is transferred to a bottle and shaken for one minute with 1% zinc amalgam. Mercury salts are thereby reduced to the metal, which dissolves in the amalgam, and iron salts are wholly reduced to the ferrous state. The liquid is then decanted from the amalgam, which is washed by decantation with two volumes of 50 c.c. of water containing dilute sulphuric acid and the whole titrated with $N/10$-permanganate.

The method described above should be a rapid and useful alternative to several more accurate but tedious processes. Three readily suggest themselves and we have carried out a few experiments on each: (1) the determination of the solubilities of metals in mercury, (2) the determination of tin and lead in solder, (3) the determination of metals electrolytically using a cathode of mercury.

Determination of Solubilities of Tin and Iron in Mercury at 15°.—To 800 g. of mercury were added 15 g. of pure tin. The solid phase was obviously present. The mixture was kept for an hour at 15° and then pressed through chamois leather three times to remove the whole of the solid phase. The amalgam was shaken with acidified permanganate in the usual way until the end-point was reached; the whole of the tin was then in solution in the

stannic form, since tin amalgam was found not to reduce stannic sulphate in measurable amount. The mass of tin in the known weight of the amalgam was then calculated from the volume and strength of the permanganate. The percentage of tin in solution in mercury at 15° was found in this way in two experiments to be 0·61 and 0·60.

A similar experiment was carried out with iron. This metal was obtained in solution by electrolysing a normal solution of ferrous sulphate containing sulphuric acid with a current of 3 amperes with a mercury cathode until the solid phase was obviously present. The solid phase was removed at 15° as with tin. Owing to the very small solubility of iron in mercury, as well as to its not being 100% efficient, the permanganate was used merely to remove the iron quantitatively from the mercury. The solution containing the iron was then treated as mentioned above and titrated with permanganate. In three experiments the solubility of iron in mercury at 15° was found to be 0·00138, 0·00140, and 0·00140%. Richards and Garrod Thomas (*Z. physikal. Chem.*, 1910, **56**, 758) found by other methods the value 0·00134 at 20°.

Determination of Tin and Lead in Solder.—The conditions necessary for success in these determinations are (*a*) that the alloy dissolves without difficulty in warm mercury, (*b*) that it has two constituents only, each of which is 100% efficient in reducing the oxidising solution used, and (*c*) that the equivalents of the metals be as widely different as possible. Solder fulfils these conditions well. A table was compiled showing the quantities of decinormal permanganate theoretically required by a gram of solder (containing lead and tin only) of varying tin composition when it is oxidised to stannic and lead sulphates. It showed that a difference in percentage composition of tin or lead of 0·1 corresponded to 0·24 c.c. of $N/10$-potassium permanganate. Since the end-point in our method can be judged with practice to about 0·2 to 0·3 c.c. of permanganate, the error of a single determination need not exceed 0·1. In practice, however, this accuracy was not always attained. In the table below, the percentage compositions of three solders obtained by the new method are compared with those determined gravimetrically.

	Percentages determined by new method.					Average values.	% determined gravimetrically.
Sn	46·4	46·3	46·5	46·3	46·4	46·4	46·4
Pb	53·6	53·7	53·5	53·7	53·6	53·6	53·6
Sn	36·4	36·3	36·1			36·3	36·1
Pb	63·6	63·7	63·9			63·7	63·9
Sn	50·7	49·8	50·0			50·2	50·5
Pb	49·3	50·2	50·0			49·8	49·5

It is seen that in the three cases the agreement is fair. A determination by the new method which includes the time taken to weigh the solder may be made in 15 minutes. We usually weighed out about 0·2 g. and this required about 60 c.c. of $N/10$-permanganate. As is to be expected from its position in the potential series, tin in the solder oxidises the permanganate before lead. This is inferred because the discoloured solution is at first clear. Later the white precipitate of lead sulphate makes its appearance. The precipitate does not obscure the end-point.

Modification of E. F. Smith's Method of Determining Metals with a Mercury Cathode.—The following metals have been found by Smith and others to be rapidly and quantitatively precipitated from solution with the use of a rotating anode and a mercury cathode : bismuth, cadmium, chromium, cobalt, copper, gold, iron, lead, manganese, mercury, nickel, silver, tin, and zinc (E. F. Smith, " Electroanalysis," 6th edition, 1919). These metals are determined by Smith's method as the difference in the weight of pure mercury before electrolysis and that of the amalgam after. With our method neither the pure mercury nor the amalgam need be weighed, so that the errors involved, especially in the second of these weighings, are avoided. On the other hand, the error of determination is greater with our method (about 0·5%) than with Smith's method when properly carried out (0·1 to 0·2%). Moreover, our method is confined to the determination of bismuth, cadmium, copper, iron, lead, manganese, tin, and zinc. The other metals named above, except chromium and cobalt, cannot be determined because they are more electronegative than mercury. Chromium cannot be determined by our method because instead of forming chromium sulphate, as is to be expected, in presence of an oxidising agent, it leaves the mercury in a finely divided state and becomes oxidised to chromous oxide. The case of cobalt has already been considered.

Rapid Method of Purifying Mercury.

A rapid method of purifying mercury from other metals may be founded on the quantitative determinations described above and is indeed obvious. It cannot be used for removing nickel or metals more electronegative than mercury, and cobalt presents some difficulty. The remaining metals more electropositive than mercury, even when in the passive state, may be removed quickly, completely, and without any loss of mercury.

If the amalgam is a concentrated one, it should be pressed twice through chamois leather to withdraw the whole of the metals in the solid phase. This lowers the concentrations of cadmium,

indium, thallium, lead, zinc, and tin to approximately 3, 2, 2, 1, 1, and 0·5%, respectively, and leaves those of copper and iron less than 0·003% (Richards and Wilson, *Z. physikal. Chem.*, 1910, **56**, 729; Richards and Garrod Thomas, *ibid.*, p. 758). The amalgam may then be placed in a stout reagent bottle and shaken vigorously with a mixture of equal volumes of 9*N*-sulphuric acid and saturated aqueous solution of potassium permanganate till it becomes discoloured. More of the oxidising solution is then added and the shaking continued till bubbles of mercury appear on the surface. The amalgam is then washed from impurities by a stream of water, and the removal of the last traces of the impure metal completed by shaking with *N*/10-permanganate acidified with 2*N*-sulphuric acid till the end-point, at which the mercury when shaken becomes a mass of small bubbles, is reached. The mercury should then be again washed by a stream of running water, shaken with 2*N*-sulphuric acid to destroy the bubbles, and pressed through chamois leather.

If *N*/10-potassium permanganate in sulphuric acid solution be used instead of the more concentrated solution the rate at which the metallic impurities are removed is slower. For small concentrations of impurities, however, this rate is not unduly slow (the removal of 0·2 g. of zinc, for example, would require about 2 minutes' shaking), and whenever the reduced solution is intended to be subsequently analysed this rate is recommended because it ensures that the end-point is not over-stepped. When the amalgam is shaken with a concentrated solution of ferric sulphate in sulphuric acid or with a mixture of this solution with permanganate, the rate at which the impurities are removed is very greatly increased. This is due to the observed fact that ferric sulphate is reduced much more rapidly than permanganate, and the greater the concentration of the ferric sulphate the more rapid is the reduction. Ferric sulphate thus catalyses the reduction of potassium permanganate and other oxidising solutions by amalgams because the former after reduction to ferrous sulphate reacts almost instantaneously with the latter and the ferric sulphate regenerated is then reduced by more of the metal of the amalgam. Using a normal solution of ferric sulphate in 2*N*-sulphuric acid, we were able, by vigorous shaking, to remove 1 g. of lead from 200 g. of amalgam in 10 seconds, and 7 g. of zinc in ½ minute. With a concentrated solution of permanganate in 6*N*-sulphuric acid and 20 c.c. of *N*/10-ferric sulphate we removed completely, by shaking in a large reagent bottle, 14 g. of a mixture of zinc, cadmium, tin, lead, solder, and bismuth from 480 g. of pure mercury, to which it had been added, without the loss of any mercury except a little removed

mechanically in washing. This fact is of interest because in the literature on the purification of mercury it is stated that when an amalgam is passed through, or shaken with, the oxidising solutions in general use, either the mercury is not completely freed from the more electropositive metals or, if it is, a considerable proportion of mercury accompanies the other metals into solution (Harries, *Z. angew. Chem.*, 1921, **34**, 359; Harries and Evers, *ibid.*, p. 541; Hulett and Minchin, *Physical Rev.*, 1905, **21**, 396).

Summary.

1. The order in which metals are removed from mercury by oxidising solutions has been determined, and is given but not discussed.

2. The reducing efficiency of amalgams of zinc, cadmium, tin, lead, copper, iron, and bismuth has been determined in solutions of ferric sulphate, potassium permanganate, and uranyl sulphate containing dilute sulphuric acid. The results are interpreted in terms of the hydrogen over-voltages of these metals.

3. The results are applied to rapid, approximate methods of determining (*a*) the solubilities of metals in mercury, (*b*) tin and lead in solder, (*c*) metals deposited by electrolysis with a rotating anode and a mercury cathode.

4. A rapid method of purifying mercury from more electropositive metals by shaking the amalgam with an oxidising agent is described. It removes such metals completely without necessarily the loss of mercury. The rate at which this purification is done may be regulated.

We wish to thank the Government Grant Committee of the Royal Society for providing us with the materials employed in this work.

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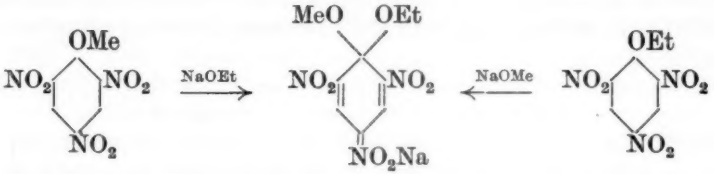
CHRIST CHURCH, OXFORD. [*Received, July 10th*, 1925.]

CCCII.—*The Alcoholysis of Trinitroanisole and Trinitrophenetole.*

By OSCAR L. BRADY and HAROLD V. HORTON.

IN connexion with other investigations it had been found that when 2 : 4 : 6-trinitro-*m*-tolyl methyl ether was crystallised from alcohol, partial conversion into the corresponding ethyl ether occurred and that when 3 : 5-dinitro-*o*-tolyl methyl ether was heated with

alcohol in the presence of alkali a similar change took place. The behaviour of 2 : 4 : 6-trinitroanisole and trinitrophenetole has now been investigated. Meisenheimer (*Annalen*, 1902, **323**, 205) has shown that the same compound is obtained by the action of sodium ethoxide on trinitroanisole and of sodium methoxide on trinitrophenetole and that this compound on decomposition with acids gives a mixture of trinitroanisole and trinitrophenetole; he proposed the following mechanism :



Similarly, Loving, Jackson, and Boos (*Amer. Chem. J.*, 1898, **20**, 444) found that when the compound obtained by the action of sodium methoxide on trinitroanisole was crystallised from ethyl alcohol, substitution of ethyl for methyl took place. Purdie and Marshall (J., 1888, **53**, 391) observed that a change of groups occurred between esters of carboxylic acids and alcohol in the presence of a small amount of sodium. The conversion can, in some cases, be carried out without the addition of sodium (Shimomura and Cohen, J., 1922, **121**, 883, 2051; see also Cohn, *Monatsh.*, 1900, **21**, 200; Lapworth and Havin, J., 1902, **81**, 1501).

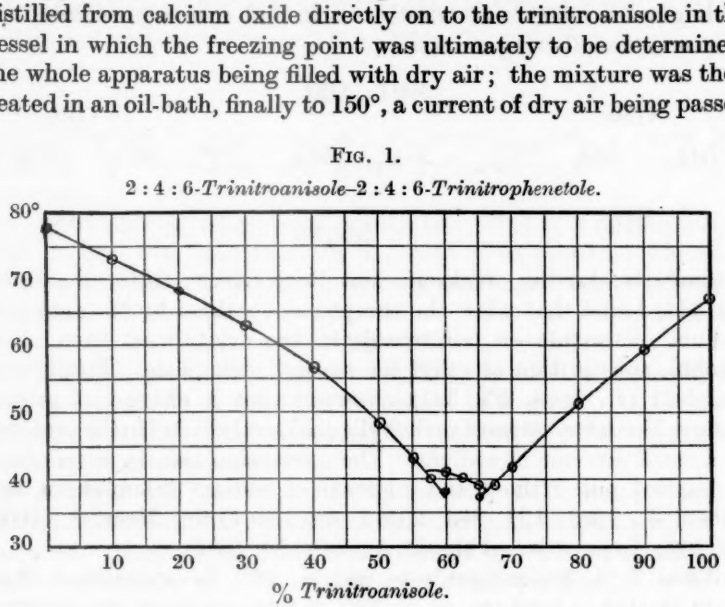
When 2 : 4 : 6-trinitroanisole (m. p. 68°) is crystallised from ethyl alcohol, a mixture, m. p. 58°, of trinitroanisole and trinitrophenetole separates, whilst trinitrophenetole crystallised from methyl alcohol gives a mixture, m. p. 52°. These observations probably account for the different values given for the melting point of trinitroanisole, namely, 48° to 64°. We have found that trinitroanisole, crystallised from dry methyl alcohol, melts in a capillary tube at 68° and freezes in bulk at 67·0°. For the purpose of analysis the binary fusion diagram of trinitroanisole and trinitrophenetole has been constructed (Fig. 1).

The two substances apparently form an unstable addition compound consisting of 3 mols. of trinitroanisole and 2 mols. of trinitrophenetole, corresponding with 58·7% of trinitroanisole. This compound does not separate readily and it is possible to prolong the left and right branches of the curve for some distance into the metastable region; in taking the time–cooling curve of a mixture containing 60% of trinitroanisole, trinitrophenetole separates at 38·0°, the temperature remains constant for some time and then rises to 41·0°, when the additive compound separates.

When a mixture of trinitroanisole (1 mol.) and absolute alcohol (10 mols.) was evaporated in an air-oven, and the residue dried at 100°, irregular results were obtained, the product having a freezing point of from 38·4° to 42·3°; it was found that picric acid had been formed owing to absorption of water by the alcohol during working. An apparatus was therefore designed in which the alcohol was distilled from calcium oxide directly on to the trinitroanisole in the vessel in which the freezing point was ultimately to be determined, the whole apparatus being filled with dry air; the mixture was then heated in an oil-bath, finally to 150°, a current of dry air being passed

FIG. 1.

2 : 4 : 6-*Trinitroanisole–*2 : 4 : 6-*Trinitrophenetole.*



over it to remove alcohol vapour. Since two layers formed as the alcohol evaporated, the mixture was stirred continuously. By this means it was found that in mixtures of alcohol and trinitroanisole in the molecular proportions of 11 to 1 and 16 to 1 conversion occurred to the extent of 16% and 22% respectively; with larger amounts of alcohol, the results were irregular, but even with 68 mols. not more than 35% of the trinitroanisole was converted into trinitrophenetole.

EXPERIMENTAL.

Preparation of Materials.—2 : 4 : 6-Trinitroanisole was prepared by two methods. 2 : 4-Dinitroanisole, prepared by the action of sodium methoxide in methyl alcohol on 2 : 4-dinitrochlorobenzene, was nitrated by Holleman's method (*Rec. trav. chim.*, 1903, **22**, 263), the nitrating mixture being heated for 3 hours at 100° and the product crystallised from methyl alcohol. Picryl chloride was treated in boiling methyl alcohol with sodium methoxide (1 equiv.) in the same

solvent, a fresh addition not being made until the colour produced by the last had almost faded. When all the sodium methoxide had been added, the mixture was diluted somewhat with water; the trinitroanisole that separated on cooling was crystallised twice from dry methyl alcohol and thus obtained pure (m. p. 68°).

Attempts to nitrate 2 : 4-dinitrophenetole to trinitrophenetole under various conditions were unsuccessful, hydrolysis occurring and picric acid being the only product isolated. Trinitrophenetole was therefore prepared from picryl chloride by the action of sodium ethoxide in a similar way to trinitroanisole (Austen, *Ber.*, 1875, **8**, 666). After experiments with thionyl chloride had proved unsuccessful, picryl chloride was prepared by a modification of Pisani's method (*Annalen*, 1854, **92**, 326). Picric acid (50 g.; larger quantities cannot safely be employed) was mixed with phosphorus pentachloride (100 g.) and heated under reflux on the water-bath. After the violent reaction had subsided, the product was poured into water and rapidly collected. After air-drying, the crude material was purified in lots of 20 g. by heating at 100° for some time with a mixture of one part of nitric acid (*d* 1·4) and four parts of sulphuric acid (*d* 1·8), cooling, pouring into water, and crystallising from a mixture of benzene and alcohol (1 : 3). The yield of pure product was about 50% of that calculated.

The freezing points of mixtures of trinitroanisole and trinitrophenetole were determined from time–cooling curves; the results are in Table I.

TABLE I.

% Trinitroanisole	0	10	20	30	40	50	55	56	57·5
F. p.	77·6°	72·6°	67·9°	62·9°	56·4°	48·1°	43·0°	42·0°	40·1°
% Trinitroanisole	60	62·5	65	67·5	70	80	90	100	
F. p.	41·0° (38·0°)	40·3°	39·4° (37·3°)	39·2°	41·7°	51·0°	59·3°	67·0°	

The figures in brackets correspond to the first arrest, where the trinitroanisole or trinitrophenetole first separated and crystallisation of the compound followed.

In conclusion, one of us (H. V. H.) wishes to thank the Department of Scientific and Industrial Research for a grant which has enabled him to take part in this work.

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CCCIII.—*The Supposed Formation of 1:2:4-Oxadiimine Rings from Nitroso-compounds and Methylenearylamines.*

By GEORGE NORMAN BURKHARDT, ARTHUR LAPWORTH, and EDWIN BREW ROBINSON.

INGOLD prepared a number of compounds by the action of nitrosobenzenes on methyleneanilines (J., 1924, **125**, 93 *et seq.*). He ascribed to the products a ring structure, $ArN<\overset{CH_2}{O}>NAr'$, and asserted that the facts were totally contrary to "the hypothesis by means of which so many obscure facts in chemistry are nowadays 'explained'" (*loc. cit.*, p. 93).

He subsequently discovered that his products were not ring compounds at all, but *N*-hydroxyamidines. In a paper with Farrow (J., 1924, **125**, 2543), he maintained, nevertheless, that cycloids are formed in the first instance and that these cycloids isomerise to hydroxyamidines at the moment of their formation (*loc. cit.*, p. 2545):

$$\left.\begin{matrix}CH_2{:}NAr\\ O{:}NAr'\end{matrix}\right\} \rightarrow ArN<\overset{CH_2}{O}>NAr' \leftarrow \left\{\begin{matrix}CH_2{:}NAr'\\ O{:}NAr\end{matrix}\right.$$

$$\downarrow$$

$$ArN(OH)\cdot CH{:}NAr'$$

The proof given was that "the substances obtained in the two ways shown by the equation above are, in each case, identical with one of the pair of isomerides prepared by Comstock and Clapp's reaction."

Only one such case, however, was described, namely, that where $Ar = C_6H_4Br(p)$ and $Ar' = C_6H_4Cl(p)$ (Ingold, *loc. cit.*, p. 101), an unsatisfactory pair in view of the close chemical relationship and likely isomorphism of their derivatives.

Farrow and Ingold also referred to the case where $Ar = C_6H_5$ and $Ar' = C_6H_4\cdot CH_3(p)$; but here the product was made in only one of the ways indicated in the above scheme, namely, from $CH_2{:}N\cdot C_6H_4\cdot CH_3(p)$ and $O{:}N\cdot C_6H_5$. It is most significant that the product was identified with $N(C_6H_4\cdot CH_3){:}CH\cdot N(C_6H_5)\cdot OH$, which on alkaline hydrolysis gave *azoxybenzene* with no trace of azoxytoluene (*loc. cit.*, p. 2551—2552) and *p*-toluidine. Here, be it noted, the aromatic radical in the original *nitroso*-compound reappears in attachment to *oxidised nitrogen* and the other, originally as methylene*amine*, as pure amine with *unoxidised nitrogen*.

Returning to the crucial case where $Ar = C_6H_4Br$ and

$Ar' = C_6H_4Cl$: a product A, made from chloronitrosobenzene and methylenebromoaniline, was identified with another, B, made from bromonitrosobenzene and methylene-*p*-chloroaniline (Ingold, *loc. cit.*), and both with a third product, C, which was made in quite a different way and certainly had the structure

$$C_6H_4Cl\cdot N(OH)\cdot CH{:}N\cdot C_6H_4Br.$$

The last-mentioned gave pure *p*-bromoaniline when hydrolysed by alkali (Farrow and Ingold, *loc. cit.*, 2551, 2552).

The present authors had good theoretical reasons for thinking it unlikely that such a ring would be formed at all in the addition process, and still more unlikely that such a ring, once formed, would break down exclusively in one direction. They therefore took up the re-examination of the product obtained by Ingold's method from *p*-chloromethyleneaniline and *p*-bromonitrosobenzene. Observing that, even after recrystallisation from benzene, the product was not very well defined, and remembering that it might be isomorphous with its isomeride (from which it differs only in the interchange of place of chlorine and bromine), they decided to hydrolyse it with aqueous-alcoholic sodium hydroxide in the general way described by Farrow and Ingold (*loc. cit.*, pp. 2547, 2548) and to examine the substituted aniline so formed. The resulting base solidified at once; even before recrystallisation it melted 67—69°, and after one crystallisation from light petroleum at 68·5—69°. (A sample of pure *p*-chloroaniline obtained from British Drug Houses Limited melted after similar treatment at 69·5—70°; and a sample of pure *p*-bromoaniline after similar treatment at 62—62·5°.)

We are indebted to Dr. E. Chapman, who has had much experience in the determination of halogen by Robertson's method, for an analysis of the base. 0·1068 Gram of the compound gave halogen equivalent to 8·23 c.c. of $N/10$-$AgNO_3$. Formula C_6H_6NCl requires 8·37 c.c. and C_6H_6NBr requires 6·21 c.c.

It is thus clear that the base was mainly *p*-chloroaniline; the authors thought they detected a very small quantity of bromine in a careful qualitative test, but this would not be very surprising, as some reduction of the bromoazo-compounds during the original hydrolysis seemed quite possible.

It is evident that a compound which yields mainly *p*-chloroaniline cannot possibly be identical with one which, as Farrow and Ingold stated, yields *p*-bromoaniline with no trace of *p*-chloroaniline. That such a mistake could ever have been made is proof that the evidence on which Ingold relied was not trustworthy and it cannot be admitted that there is any good reason to suppose that his cycloids are formed at any stage.

If Farrow and Ingold are disposed to maintain their original view, then the onus of proof rests with them. An obvious and acceptable line of proof would be for them to prepare their compounds by both the methods in the scheme on p. 2234 and to show that these then give the same products in the same proportion when hydrolysed.

In conclusion, the facts, so far as they have yet been fully established, are entirely consistent with polarity theories, all previous statements to the contrary notwithstanding (*inter alia*, Ingold, J., 1924, **125**, 93; Ingold and Weaver, *ibid.*, pp. 1457—1459).

THE UNIVERSITY, MANCHESTER. [*Received, June 18th*, 1925.]

CCCIV.—*The Properties and Constitution of Coal Ulmins. Studies in the Composition of Coal.*

By WILFRID FRANCIS and RICHARD VERNON WHEELER.

WE have demonstrated (this vol., p. 112) that bituminous coal consists essentially of a matrix of insoluble ulmins in which morphologically organised plant tissues and natural plant-substances devoid of morphological organisation, that have escaped ulmification, are dispersed; * thereby confirming conclusions reached from other considerations (Tideswell and Wheeler, J., 1922, **121**, 2345; 1925, **127**, 110). In some bituminous coals the proportion of plant entities, chiefly cuticles and spore exines, is as high as 20% by weight, but in all bituminous coals the ulmins form the predominant material. Knowledge of their properties and constitution is therefore essential to an understanding of the composition of coal. We have sought to obtain this knowledge by both synthetic and analytical means. The present paper deals with the results of our analytical studies.

The chief effect of mild oxidation on bituminous coal is to change the matrix of ulmins from a form insoluble in dilute alkalis to a soluble form, thereby allowing of their separation from the organised plant material associated with them and rendering possible their examination by the usual methods of organic analysis. Suitable

* The matrix is not structureless, as was originally supposed, but close examination discloses, even in material selected as being a vitrain, a more or less pronounced structure, usually of woody tissue, such as a theoretically perfect vitrain should not possess. Such structures cannot, however, be separated from the coal mass intact, as can the cuticles and spore-exines, and they are ulmified.

mild oxidation can be effected by such reagents as hydrogen peroxide, or by exposure to air at 150°.

No fundamental change in the structure of the ulmin molecule is made by such a mild oxidation, but the external groupings are modified, those most readily detached being eliminated as simple oxygenated compounds and their place being taken by carboxylic groupings. The internal or nuclear arrangement of the molecule of the soluble " regenerated " ulmin (*loc. cit.*, p. 123) is thus identical with that of the insoluble matrix of unoxidised bituminous coal, and from a knowledge of the constitution of the former the essential structure of the main mass of bituminous coal can be deduced.

The change from insoluble to soluble ulmins is a gradual one. A moderate degree of oxidation will produce sufficient change in the external groupings of the ulmin molecule to render the matrix of bituminous coal soluble with difficulty in alkalis. As oxidation proceeds, more groupings are eliminated and the ulmins become more acidic in character and more readily soluble in alkaline or neutral solvents. A limiting condition is, however, eventually reached when all suitable external groupings have been eliminated. (In this connexion, compare Pearson, *J. Soc. Chem. Ind.*, 1923, 42, 68T.) This stage is reached on oxidation by air at low temperatures. Further, carefully regulated, oxidation by hydrogen peroxide or nitric acid can cause a breakdown of the nuclear structure of the ulmin molecule and it is by the identification of any simpler compounds resulting from such a breakdown that the character of the nucleus of the complicated ulmin molecule can be revealed.

The Properties of Regenerated Ulmins.—Because the changes produced in bituminous coal by mild oxidation are gradual, the soluble ulmins produced are not homogeneous. They can be separated into a number of fractions by means of different solvents; but all the fractions are compounds of the same type and differ but slightly one from another in their analysis. We have not considered it necessary to effect a separation of them for the major portion of the work described in this paper.

The carboxyl groups produced by oxidation give to the soluble ulmins a definite acidic character allowing of salt formation. Amongst the insoluble salts that we have prepared are those of barium, iron, silver and copper. From the last-named an average value of 170 for the equivalent of the ulmins has been obtained, a figure which should be compared with that given by Sven Odén, namely, 350, for soil ulmins (*Proc. Faraday Soc.*, 1921). No convenient method is at present available for determining the molecular weight (if the colloidal character of the substances admits of such

a determination), but from the value of the equivalent an expression can be given of the contents of such determinable groupings as hydroxyl and carboxyl, and of nitrogen. The presence of hydroxyl groups has been proved by acetylation and benzoylation and by Grignard's reaction. By hydrolysis of the acetyl derivatives the percentage of hydroxyl groups in the "regenerated" ulmins as an average has been found to be 2·5, or one hydroxyl group for each molecular unit of 680. Such a unit would contain four carboxyl groups, a supposition confirmed by a quantitative estimation of the methane evolved from the dry ulmin on treatment under suitable conditions, with Grignard's reagent.

It is significant that as the oxidation of coal proceeds, with the gradual formation of soluble ulmins, the nitrogen-content increases up to the point at which the whole of the coal matrix becomes soluble. Moreover, all the slightly modified types of regenerated ulmins that can be separated by means of organic solvents contain nitrogen in the same proportion. This element must therefore be an essential constituent of the nucleus of the ulmin molecule.* The percentage of nitrogen found, 2·20—2·25, would indicate the presence of one nitrogen atom in the molecular unit suggested.

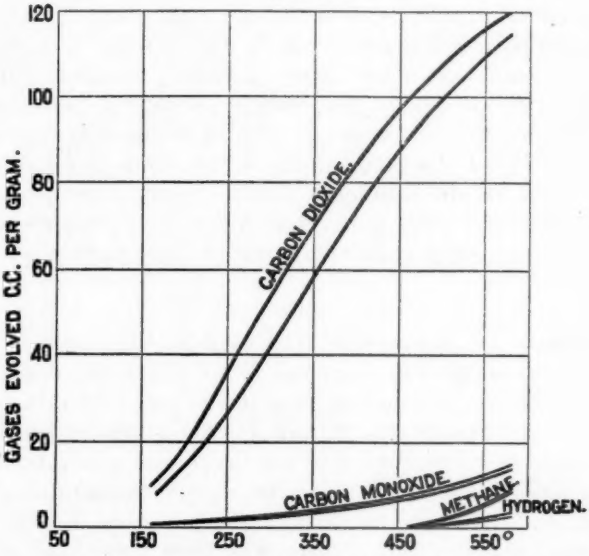
The presence of nitrogen as an essential constituent of the molecule renders it necessary to take account of this element in any theory regarding the origin of the coal-ulmins and lends particular interest to the reaction between amino-acids and sugars discovered by Maillard (*Ann. Chim. Phys.*, 1916, **5**, 258; 1917, **7**, 113) which results in the formation of ulmins. In the coal-forming process, from plant debris, the sugars may be derived from the celluloses of the cell-walls by enzyme or bacterial action and the amino-acids from the polypeptides in the protein matter of the cell contents. These reactions, whereby it is conceivable that the matrix of coal can be synthesised, are being studied by Mr. T. A. Buckley.

Some information as to the character of the external groupings of the molecule of the regenerated ulmin is given by the results of regulated destructive distillation. On heating the ulmins in the manner described in the experimental portion of this paper, gas began to be evolved in small quantity at 160—170°. This gas consisted of the oxides of carbon in ratio CO_2/CO of 12 : 1. This ratio increased up to 300° and then rapidly decreased. Measurable quantities of hydrogen and saturated hydrocarbons were not evolved until about 450°. Water accompanied the oxides of carbon at the lower temperatures of distillation, but no other

* A similar conclusion is to be drawn from the experiments of Monkhouse and Cobb (*Trans. Inst. Gas. Eng.*, 1922) on the action of steam on coke.

liquid made its appearance until 550°, when a slight trace of oil could be detected. These results correspond in general character with those obtained with the peat ulmin, dopplerite (Tideswell and Wheeler, J., 1922, **121**, 2345). The striking similarity of the curves relating the evolution of gases with temperature (Fig. 1), obtained with ulmins prepared from a vitrain and a durain respectively, confirms the deductions previously made (*loc. cit.*) that the matrix of a durain is essentially the same as that of a vitrain (or a clarain), differing from it only as regards the character of the less important external groupings of the molecules.

FIG. 1.



Destructive distillation of regenerated ulmins. For each gas the upper curve relates to a vitrain ulmin and the lower to a durain ulmin.

The Constitution of the Regenerated Ulmins.—By breaking down the nucleus of the molecule, by the cautious use of hydrogen peroxide or dilute nitric acid, simpler compounds can be obtained, the identification of which gives information as to the groupings within the nucleus. A number of such compounds have been identified.

The extreme action of hydrogen peroxide on the regenerated ulmins results in the formation of water and the oxides of carbon, the nitrogen appearing quantitatively as ammonia. Intermediate action yields aliphatic dibasic acids, of which oxalic and succinic have been isolated in pure crystalline form, together with a number of acids having all the properties of benzene polycarboxylic acids.

The isolation and identification of all these acids can, however, more readily be effected by the use of dilute nitric acid, which yields water-soluble products, amounting to about 25% of the regenerated ulmin, consisting of aliphatic dibasic acids, aromatic acids and nitrophenols. The products so far isolated and identified are oxalic, succinic, picric and pyromellitic acid (benzene-1 : 2 : 4 : 5-tetracarboxylic acid), whilst there is evidence of the presence of trimellitic acid. (Fischer and Schrader, *Brennstoff-Chem.*, 1921, **2**, 213, obtained traces of aromatic carboxylic acids by the pressure oxidation of a bituminous coal at 200—250°.)

The identification of picric and pyromellitic acids proves beyond question the presence of benzenoid rings in the nucleus of the regenerated ulmin molecules, and hence in the matrix of bituminous coal, for no part of our treatment of the coal has been such as to cause ring formation where none previously existed. Since such aliphatic acids as oxalic and succinic have also been obtained, whilst the nitrogen is clearly present in stable ring formation, it can be concluded that the nuclei of the ulmin molecules—which form the bulk of all bituminous coals—consist of compact systems of benzenoid groupings connected together by heterocyclic ring structures, such as pyrrole and furan or their derivatives.

Experimental.

Preparation of Regenerated Ulmins from Bituminous Coal.—A vitrain was usually employed so as to avoid the complications introduced by the presence of plant debris and to obtain the maximum yield of ulmins. The vitrain was finely ground and added to three times its weight of 100 vol. hydrogen peroxide. After a few minutes the mixture began to rise in temperature and the reaction tended to become violent. To moderate it, cold distilled water was added. The mixture was then heated at about 90° during several hours. The soluble ulmins thus formed were extracted with dilute sodium hydroxide solution and the residue was re-treated with hydrogen peroxide, the processes being repeated until no residue remained.

As thus prepared, soluble ulmins from the vitrain of East Kirkby coal contained C 68·8 and H 3·9%. Successive treatments of this material with hydrogen peroxide caused a reduction in the carbon and hydrogen contents until a limiting composition C 62·5 and H 2·8% was reached, similar figures being obtained with all the coals examined (whether vitrains, clarains, or durains). In obtaining this limiting composition, however, some destruction of the ulmins occurred and, since for subsequent examination a large yield rather than a homogeneous material was required, the usual

procedure was to check the oxidation as soon as solubility was attained.

Solubility of the Regenerated Ulmins.—The non-homogeneous ulmins so obtained were fractionated by means of solvents and each fraction was examined separately. The solvents used, at their respective boiling points, were: Chloroform, ethyl alcohol, acetone, methyl ethyl ketone, pyridine, pentane, light petroleum, benzene, ether, and carbon disulphide. Only the first five of these had any marked solvent action. In Table I the percentage amounts extracted by each solvent, in the order named, from a number of samples of regenerated ulmins are recorded.

TABLE I.

Solubility of Regenerated Ulmins.

	Source of Regenerated Ulmin.					
	East Kirkby vitrain.			East Kirkby vitrain α-compounds.*		
Solvent.	Sample A.	Sample B.	East Kirkby durain.	Sample A.	Sample B.	Hamstead vitrain.
Chloroform	0·4	0·4	0·3	0·4	—	—
Alcohol	7·2	2·2†	7·5	6·4	40·2	28·0
Acetone	3·8	12·2†	4·5	5·4	9·0	5·0
Me Et ketone ...	—	4·3	—	—	—	—
Pyridine	33·0	42·0	38·5	36·0	23·0	19·5

* The term α-compounds refers to that portion of the coal that was insoluble in pyridine.

† Order of extraction reversed.

All the ulmins, except sample B from the East Kirkby vitrain α-compounds and the sample from the Hamstead vitrain, were obtained as soon as the treatment with hydrogen peroxide rendered the coals soluble in alkalis. The two exceptions were subjected to more prolonged oxidation. Analyses of many of these fractions are given in Table II.

TABLE II.

Analyses of Fractionated Ulmins. Per cent. on ash-free dry material.

Ulmins prepared from : Fraction.	Carbon.	Hydrogen.	Oxygen and nitrogen (by difference).
East Kirkby vitrain, alcohol-sol.	64·4	5·1	30·5
„ „ acetone-sol.	66·6	4·9	28·5
„ „ pyridine-sol.	68·3	4·5	27·2
„ „ α-compounds alcohol-sol.	65·5	4·8	29·7
„ „ α-compounds acetone-sol.	65·6	4·6	29·8
Hamstead vitrain, alcohol-sol.	63·8	4·1	32·1
„ „ pyridine-sol.	65·5	3·7	30·8

It will be seen that the compounds were all of the same type, the different degrees of solubility being caused presumably by slight modifications in the external groupings of the molecules. The amount extracted by each solvent depended upon the order of extraction and each fraction was to some extent soluble in the other solvents. In general it was found that the further oxidation with hydrogen peroxide had been carried the more soluble in such neutral solvents as alcohol and acetone were the products.

The Preparation of Salts and Determination of the Equivalent.—Well-defined salts of barium, calcium, silver and copper were formed by the addition of a soluble salt of the metal to an ammoniacal solution of the ulmin. The copper salt was used to determine the equivalent. For its preparation, excess of a boiling ammoniacal solution of copper hydroxide was added to the boiling ulmin solution, the mixture well stirred and allowed to cool. The precipitate, which formed readily, was washed several times by decantation, filtered off and washed free from copper hydroxide with dilute ammonia and finally with distilled water. The equivalent was calculated from the analysis of the dried salt and found to be: East Kirkby vitrain ulmin, 171; East Kirkby vitrain ulmin, fraction insoluble in pyridine, 164; East Kirkby vitrain α-compound ulmin, 165.

Examination for Hydroxyl and Carboxyl Groups.—The presence of these groups in the regenerated ulmins was proved by the formation of an acetyl derivative, using acetic anhydride and sodium acetate, and by the formation of a benzoyl derivative, using benzoyl chloride in pyridine solution. The acetyl derivative was used to estimate the content of hydroxyl by determining the amount of acetic acid liberated on hydrolysis and steam distillation with benzenesulphonic acid. The ulmin from Hamstead vitrain was found to contain hydroxyl equivalent to 2·6%; and that from the East Kirkby vitrain 2·4%.

Estimation of the total hydroxyl, including that in carboxyl groupings, was made by the use of Grignard's reaction, 13·4% being found; whence the number of carboxyl groups is four times that of free hydroxyl groups. As was to be anticipated, methoxyl groups were not present.

Nitrogen Content.—During the production of regenerated ulmins by atmospheric oxidation there was a gradual increase in the nitrogen content of all the coals examined until a proportion of 2·25% was reached. This figure was confirmed on analysis of the ulmins produced by the action of hydrogen peroxide. From whichever coal they were formed, and whichever solvent fraction was taken, the nitrogen content was about 2·25%. From this it

appears that most of the nitrogen of the ulmins (and of coal) resides in the nuclear groupings, which mild oxidation does not attack. Moreover, since there must be at least one nitrogen atom per molecule, it follows that the average molecular weight of the regenerated ulmin is not less than about 680. Suitable tests showed that the nitrogen was present in limited amount (not more than about 0·2%) as $-NH_2$ and $-N{\cdot}CH_3$, but the greater proportion was inert, suggesting that its chief mode of occurrence is in a closed ring compound. On the complete breakdown of such a ring, by the extreme action of hydrogen peroxide, the nitrogen is evolved quantitatively as ammonia.

Destructive Distillation.—One gram of the regenerated ulmins prepared from the East Kirkby vitrain and durain respectively was destructively distilled in a horizontal glass tube attached to a Sprengel mercury pump. The temperature was raised by stages of 50°, each temperature being maintained constant during 24 hours or until all gas had ceased to be evolved. The results of examination of the gaseous products are recorded in Tables III and IV.

Explosion analysis in each instance showed the paraffin hydrocarbon present to be methane only.

In Fig. 1 the volumes of the principal gases evolved per gram of material are plotted against temperatures of decomposition. These curves should be compared with that obtained by Tideswell and Wheeler (*loc. cit.*) on the destructive distillation of the peat ulmin, dopplerite.

Oxidation of Regenerated Ulmins.—The action of hydrogen peroxide on the regenerated ulmins was in some instances continued with the intention of breaking down the nucleus of the large ulmin-molecule, so as to obtain compounds of smaller molecular weight from which the internal structure of the ulmins could be deduced. The intense action of hydrogen peroxide was difficult to regulate, resulting most often in the production of water, ammonia and the oxides of carbon, many compounds, the isolation of which would have been of value, having only a transient existence. Nevertheless, good yields of oxalic and succinic acids were obtained and separated by fractional crystallisation. Other crystalline products, apparently polybasic acids, await identification. In addition, small quantities of acids have been obtained having all the properties of benzene polycarboxylic acids.

A more satisfactory reagent with which to effect the breakdown of the regenerated ulmin molecule, since its action could more readily be controlled, was found to be 30% nitric acid. The reaction was carried out in a flask with reflux condenser, at first without external heat and later by boiling during 12 hours. The soluble products

Table III.

Destructive Distillation of Regenerated Ulmins from East Kirkby Vitrain.

(One gram of material, containing 2·1% of ash.)

Temperature range	15—160°	160—210°	210—260°	260—310°	310—360°	360—410°	410—460°	460—510°	510—580°
Volume of gas evolved (c.c. at N.T.P.)	10·25	12·25	20·0	18·5	16·15	15·5	14·5	19·5	20·5
Analysis %:									
CO_2	92	91·3	94·6	94·7	91·2	88·4	83·9	61·9	40·4
CO	8	7·8	4·8	4·8	6·8	8·5	10·8	16·2	18·6
C_nH_{2n}	—	—	—	—	2·0	0·2	0·7	1·4	0·2
C_2H_4	—	—	—	—	—	0·5	0·9	1·6	0·4
H_2	—	—	—	—	—	2·4	0·8	4·8	11·5
CH_4	—	—	—	—	—		3·0	14·1	28·9

Table IV.

Destructive Distillation of Regenerated Ulmins from East Kirkby Durain.

(One gram of material, containing 2·5% of ash.)

Temperature range	15—170°	170—220°	220—270°	270—320°	320—370°	370—420°	420—470°	470—520°	510—580°
Volume of gas evolved (c.c. at N.T.P.)	8·2	8·6	14·5	16·0	20·0	14·5	18·0	18·5	20·0
Analysis %:									
CO_2	93	92·6	94·2	93·8	90·4	89·4	82·0	69·0	47·4
CO	7	6·9	5·4	5·2	7·4	8·3	11·6	14·5	18·2
C_nH_{2n}	—	—	—	—	0·2	0·4	0·5	1·5	—
C_2H_4	—	—	—	—	0·5	0·6	1·2	0·4	—
H_2	—	—	—	—	1·4	1·3	0·4	3·2	7·0
CH_4	—	—	—	—			4·2	11·4	27·4

were then distilled in steam, the distillate containing acetic acid. The residue was heated on a water-bath to remove the last traces of nitric acid, the product thus obtained being a pale yellow, spongy mass, completely soluble in ether and amounting to about 25% of the original ulmin. By benzene extraction, picric acid, 3% on the original ulmin, was obtained, its identification being effected by the method of mixed melting points and by the preparation of a naphthalene derivative, m. p. 149°.

By means of their lead, silver and barium salts the remainder of the soluble products of the action of nitric acid on regenerated ulmins were separated. Oxalic acid was obtained in pure crystalline form, whilst other products, nearly pure but difficult to crystallise, were benzene tri- and tetra-carboxylic acid. Symmetrical benzene-tetracarboxylic acid (m. p. 264°, with decomposition) has been isolated in a pure form by slow crystallisation from acetic acid, and its methyl ester, m. p. 138°, formed. The tricarboxylic acid appears to be trimellitic acid, but it has not yet been obtained in sufficiently pure crystalline form to identify.

The presence of picric acid and these benzene polycarboxylic acids in the products, whilst proving the existence of aromatic nuclei in coal, does not necessarily confirm the theory of Fischer and Schrader (*Brenn. Chem.*, 1922, **3**, 161) as to the origin of coal exclusively from lignin; for Marcusson's explanation (*Ber.*, 1921, **54**, 542) of the formation of ulmins from sugars through furfural as an intermediary equally allows of there being benzene nuclei in the products, the condensation of the furfural derivative to a *peri*difuran compound resulting in a substance containing both furan and six-membered rings.

The work of isolating further compounds resulting from the breakdown of regenerated ulmins from bituminous coal is being continued. Our thanks are due to the Safety in Mines Research Board for permission to publish these results.

SAFETY IN MINES RESEARCH BOARD LABORATORIES,
SHEFFIELD. [*Received, July 25th*, 1925.]

CCCV.—*The Coagulation of a Colloidal Solution by Hydrogen Ions.*

By ALAN B. WEIR.

INVESTIGATIONS have been recently carried out in America into one of the chief problems met with in the study of the precipitation of suspensions, emulsions, and colloidal solutions by electrolytes;

namely, whether the active agent is the ion carrying a charge of sign opposite to that of the colloid particles, or whether there is a peptising or stabilising effect due to the other electrolyte ion, the charge of which is of the same sign as that carried by the colloid.

Tartar and Gailey (*J. Amer. Chem. Soc.*, 1922, **44**, 2212) studied the precipitation of gamboge and mastic suspensions, in the first case by acids. These are negative suspensions, and the active agent should therefore be the hydrogen ion. The minimum concentration of acid for complete precipitation of the suspensions was found in the case of five acids: hydrochloric, sulphuric, oxalic, acetic, and phosphoric. The amounts of acid required differed considerably from acid to acid, but the hydrogen-ion concentration of the supernatant liquid, *i.e.*, of the medium from which coagulation had just taken place was, "within the limits of experimental error," the same in each case. The conclusion drawn from these and further experiments described in the same paper was that the "so-called stabilising effect" of the anion (on negative suspensions) could not be detected, and, further, that the irregularities often attributed to this effect were due, even in the case of coagulation by neutral salts, to the important factor of hydrogen-ion concentration.

Bradfield (*J. Amer. Chem. Soc.*, 1923, **45**, 1243), using a clay suspension, confirmed these results for several acids, which precipitated at an almost uniform p_H of 3·8, but found that citric acid was consistently abnormal, requiring a p_H of 3·2.

The author has therefore investigated the applicability of this rule to a true colloidal solution of negative sign, noting whether the abnormality of citric acid recurred.

Experimental.

The sol chosen was one of Prussian blue, as preliminary work on various arsenious sulphide sols showed that they could not be completely precipitated either with citric or acetic acid.

The sol was prepared by slowly adding 0·4 g. of potassium ferrocyanide, dissolved in 20 c.c. of water, to 0·4 g. of ferric chloride in 20 c.c. of water, filtering off the dye, washing, peptising with a solution of oxalic acid (16 g. in 300 c.c. of water), and dialysing till free from oxalic acid. The sol was then diluted to 700 c.c.

Procedure.—The precipitation of the sol by four acids, hydrochloric, sulphuric, acetic, and citric, was examined. The minimum concentration of each acid required for complete coagulation of the sol was found in the usual manner. Graded amounts of the stock acid solutions were placed in test-tubes and accurately diluted to 10 c.c., then 10 c.c. of the sol were added, the whole was mixed

by pouring, and kept for 48 hours (for this sol flocculates slowly). The amounts of the acids required (per 20 c.c. of mixture) were thus found with an accuracy of 0·1 c.c.

In the case of the four critical concentrations, the supernatant liquid, after the dye had been precipitated, was poured off, and its hydrogen-ion concentration ascertained by means of a Clark hydrogen electrode. For standards, saturated and $N/10$-calomel electrodes were used.

In order to see whether any pronounced adsorption of the acid on the colloid had taken place, identical acid mixtures were similarly examined in absence of any colloid, *i.e.*, with 10 c.c. of water substituted in each case for the 10 c.c. of sol used previously.

Acid.	Conc. in milli-equivs. per litre.	p_H of medium after precipitation.	p_H of acids alone.
Hydrochloric	17·1	1·88	1·80
Sulphuric	26·0	1·80	1·73
Acetic	1800	2·27	2·17
Citric	642	1·91	1·83

The results show: 1. An agreement in p_H values, in the case of three of the acids, which is as good as has yet been attained by this method. Such discrepancy as exists the author believes to be due to the difficulty of deciding whether "complete precipitation" has taken place or not, which might be overcome by the use of some form of colorimeter.

2. That citric acid appears to behave normally, contrary to what was found by Bradfield.

3. That some adsorption, either of hydrogen ions or acid molecules, on the precipitating colloid has taken place (compare third and fourth columns).

4. That acetic acid precipitates at a p_H distinctly lower than that of the other acids. This may be due either to a specific adsorption of the anion, or to the action of the undissociated acid molecules present at such a relatively high concentration.

Effect of the Oxalic Anion.—In the usual preparation of Prussian blue sols the dye is peptised by a solution of oxalic acid. A strong specific adsorption of the oxalic ion is inferred. Consequently, precipitation of such sols by means of oxalic acid solutions would not be expected. The sol already studied was not affected at all by concentrations of oxalic acid up to 100 milli-equivs. per litre. With the object of investigating the effect of the oxalic ion, a Prussian blue sol was prepared without the aid of oxalic acid, and its precipitation carried out. The dye was prepared exactly as before, thoroughly washed, and a sol obtained by repeatedly grinding the solid with water and filtering. The sol was dilute,

but perfectly stable after standing for 3 weeks. Analysis showed it to contain 0·072 g. of solid per litre. The stock solutions were *N*-oxalic and 0·11*N*-hydrochloric acid, and the technique was the same as that described above. Precipitation by oxalic acid occurred at a high, but quite definite concentration, whereas only a very small amount of hydrochloric acid was required. The p_H of the precipitating medium was observed as before.

Acid.	Conc. in milli-equivs. per litre.	p_H of medium after precipitation.
Hydrochloric	1·1	2·63
Oxalic	303 to 404	0·91 to 0·79

In the case of oxalic acid, precipitation was partial at the lower, but complete at the higher, concentration. The critical concentration lies between these two values. At a concentration of 202 milli-equivs. of oxalic acid per litre the sol showed no signs of precipitation after several days.

In view of the peptising effect of this acid, already referred to, the possibility of its use as a precipitant is interesting. Once precipitated by this acid, the dye could not be peptised by shaking with the precipitating mixture, whereas precipitates produced by other acids were readily peptised by adding a solution of oxalic acid and shaking.

In the high concentration and p_H values which oxalic acid demands for flocculation of the dilute sol, a strong protective adsorption of the anion is indicated.

My thanks are due to Mr. A. E. Clarence Smith for his advice and assistance.

UNIVERSITY COLLEGE, SOUTHAMPTON. [*Received, July 25th,* 1925.]

CCCVI.—*The Constitution of the Thionic Acids.*

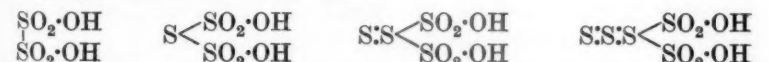
By ISRAEL VOGEL.

ALTHOUGH the problem of the constitution of the thionic acids has occupied the attention of many investigators (compare Fordos and Gelis, *Compt. rend.*, 1842, **15**, 920; Blomstrand, "Chemie der Jetztzeit," p. 157; Mendeléev, *Ber.*, 1870, **3**, 870; Michaelis, *Annalen*, 1873, **170**, 37; Spring, *Ber.*, 1874, **7**, 1161; Debus, J., 1888, **53**, 280; Hertlein, *Z. physikal. Chem.*, 1896, **19**, 286; Riesenfeld and Feld, *Z. anorg. Chem.*, 1921, **119**, 225; Martin and Metz, *ibid.*, 1923, **127**, 82; Benrath, *Z. angew. Chem.*, 1922, **35**, 33; Raschig, "Schwefel und Stickstoffstudien," 1924, p. 305; Vogel, *Chem. News*, 1924, **128**, 325, **343**, **361**; Vogel, Thesis, 1925, University of London; the last-named contains a complete review of

the literature), it cannot be said that a final or even a satisfactory solution has yet been attained.

In the course of an investigation of sulphur sesquioxide (Vogel and Partington, this vol., p. 1514) it became evident that none of the formulæ hitherto proposed could give a rational explanation of the experimental facts recorded therein. For example, the gradual increase with time of the relative quantities of tetra- and pentathionates in the products obtained by the interaction of sulphur sesquioxide with water, with sodium ethoxide, and with the blue solution obtained by the dissolution of sulphur in 65% oleum, respectively, and also the almost exclusive formation of trithionate in the reaction between concentrated potassium acetate solution and a solution of sulphur sesquioxide in oleum, were some of the facts for which an explanation had to be found. In addition to these, the liberation of *two* atoms of sulphur from pentathionates by bromine and by mercuric cyanide (Debus, *loc. cit.*), and by mercuric chloride (Sander, *Z. angew. Chem.*, 1916, **29**, 11; compare Riesenfeld and Feld, *loc. cit.*), the separation of *one* atom of sulphur from pentathionates on treatment with cold sodium carbonate solution (Raschig, *op. cit.*, p. 273), the conversion of tetrathionates into pentathionates by acidified sodium thiosulphate solution and the formation of dithionates by the action of acid potassium permanganate solution on trithionates (Raschig, *op. cit.*), the strong acidity of the thionic acids and the non-formation of complex-ions with mercury or silver salts (Hertlein, *loc. cit.*), the difference in refractivity corresponding to bivalent sulphur between two consecutive thionates, *e.g.*, between $K_2S_4O_6$ and $K_2S_5O_6$, are some of the chief experimental facts the interpretation of which is not possible on any one set of formulæ.

The following formulæ, which are in agreement with experiment, are proposed for the thionic acids:



Dithionic acid. Trithionic acid. Tetrathionic acid. Pentathionic acid.

It might be of interest, in view of the controversy as to the relative stabilities of the thionic acids (compare Riesenfeld and Feld, *loc. cit.*; Foerster and Hörnig, *Z. anorg. Chem.*, 1922, **125**, 86), to point out that according to the above formulæ the relative stabilities should decrease in the order di-, tri-, tetra-, and pentathionic acid. This is in accord with the thermochemical measurements of Martin and Metz (*ibid.*, 1923, **127**, 83).

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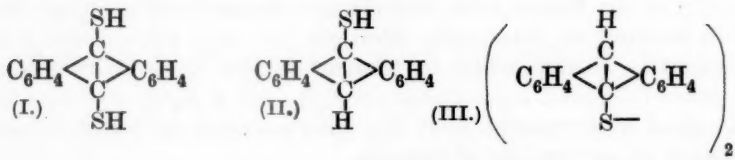
[*Received, August 5th*, 1925.]

CCCVII.—meso-*Thioanthracene Derivatives. Part II. Dianthranyl Disulphide and Dianthranyl Tetrasulphide.*

By WILLIAM HERBERT COOKE, ISIDOR MORRIS HEILBRON, and GEORGE HUGH WALKER.

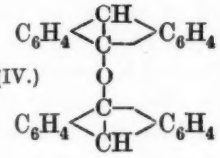
THE action of the equivalent amount of sodium hydrosulphide (2 mols.) upon 9 : 10-dibromoanthracene in amyl-alcoholic solution has been shown (Heilbron and Heaton, J., 1923, **123**, 173) to give rise to a complex series of *meso*-thioanthracene derivatives, but the conditions attending the production of any particular compound were obscure, as successive precisely similar experiments did not invariably lead to the same substances. In continuing this investigation, the effect of employing a large excess of sodium hydrosulphide (4 mols.) was first studied, as it was hoped thus to be able to isolate the disodium salt of the hypothetical 9 : 10-dithiolanthracene (I), which, as previously stated, is to be regarded as the initial product. Actually, however, the reaction proceeded in a wholly different direction, the product containing 30—40% of dianthranyl disulphide (III) (Friedländer and Simon, *Ber.*, 1922, **55**, 3969).



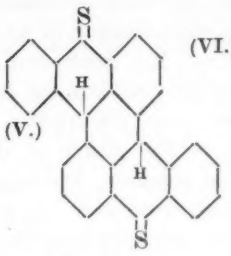
The presence of this compound in such large quantities harmonises well with the view that 9 : 10-dithiolanthracene truly represents the first stage in the reactions. Its formation is doubtless the result of reduction of the dithiolanthracene to 9-anthranyl mercaptan (II) during the course of the reaction, followed by oxidation of the latter substance to the disulphide during the working-up process (see experimental part). In addition to dianthranyl disulphide a compound containing neither sulphur nor halogen was isolated and to this the structure (IV) has been assigned on the grounds that on reduction it yields both anthranol and anthracene. It is probably formed from 9-anthranyl mercaptan by hydrolysis and is the oxygen analogue of the dianthranyl sulphide (*loc. cit.*).

The effect of employing less than one equivalent of sodium hydrosulphide was the production of a large quantity of dithioheptacyclene (V) (80—90% yield); which is invariably produced

in 10% yield when equivalent quantities of sodium hydrosulphide and 9 : 10-dibromoanthracene are employed (*loc. cit.*).

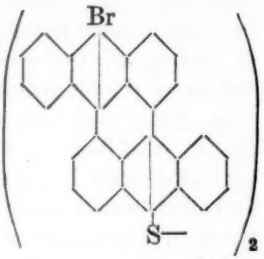


(IV.)



(V.)

(VI.)

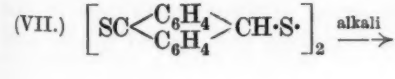


The effect of sodium sulphide, sodium disulphide, and sodium polysulphides upon dibromoanthracene has also been examined.

Sodium sulphide. When the equivalent quantity of this salt was used, the dibromoanthracene ceased to separate from the amyl-alcoholic solution after 3 days' continuous boiling; the products were unchanged material and small quantities of dianthranyl disulphide and anthracene. Even when a considerable excess of sodium sulphide was present, very little change was noted on simply boiling the reactants under reflux, but on heating in an autoclave for 2 hours at 150°, the dibromoanthracene was completely converted into dithioheptacyclene.

Sodium disulphide. On refluxing a solution of the reactants in amyl or butyl alcohol the dibromoanthracene rapidly disappeared; after 8 hours, the solution was deep red and addition of small quantities of water precipitated practically pure dianthranyl disulphide (average yield: 60%). When ethyl alcohol was used as solvent, dibromoanthracene was recovered even after 3 days' boiling. On the other hand, by heating the reactants with amyl alcohol in an autoclave for 4 hours at 200° a yellow, amorphous compound (insoluble in all media) was formed to which the constitution (VI) has been tentatively assigned. Its formation may be attributed to a fusion of the anthracene molecules with loss of hydrogen bromide in an analogous manner to that leading to dithioheptacyclene.

Sodium polysulphides. On treatment of 9 : 10-dibromoanthracene in boiling amyl-alcoholic solution with this mixture of salts, in which the tetrasulphide is probably the main constituent, a good yield was obtained of the substance to which Heilbron and Heaton (*loc. cit.*) had assigned the dithiodianthrone disulphide structure (VII) on the grounds that it was soluble in boiling alcoholic potash,

(VII.)  (VIII.)

supposedly existing in the solution as the potassium salt of the tautomeric dithiodianthranol derivative (VIII). Owing to the ease with which this substance can now be obtained, it has been possible to make a more detailed examination of its properties. The action of boiling alcoholic potash has been confirmed in so far as the substance dissolves completely on boiling, forming a blood-red solution. In no case, however, could the original compound be recovered, for on acidification by means either of dilute acetic acid or of carbon dioxide in ice-cold solution, hydrogen sulphide was evolved and dianthranyl disulphide produced. It is impossible to reconcile the ready formation of the disulphide in this way with the structure (VIII), and it would appear that the true constitution of this compound is that of an organic tetrasulphide the structure of which could be expressed by one or other of the following formulæ :

$C_{14}H_9 \cdot S \overset{\|}{\underset{S}{\cdot}} S \cdot C_{14}H_9$ (IX.) $\quad C_{14}H_9 \cdot S \cdot S \overset{\|}{\underset{S}{\cdot}} S \cdot C_{14}H_9$ (X.) $\quad C_{14}H_9 \cdot S \cdot S \cdot S \cdot S \cdot C_{14}H_9$ (XI.)

Holmberg (*Annalen*, 1907, **359**, 81), in a critical review of the structure of organic tetrasulphides, comes to the conclusion that the straight-chain type is the most probable, and in the case of the compound under review, (XI) is wholly in keeping both with its method of formation and with its ease of decomposition. Again, an attempt to form a methiodide by boiling the dianthranyl tetrasulphide with methyl iodide failed, and this is in agreement with the results obtained by Smythe and Foster (J., 1910, **97**, 1197) in their work on benzyl tetrasulphide.

Experimental.

Treatment of 9 : 10-*Dibromoanthracene with Excess of Sodium Hydrosulphide.—Dianthranyl disulphide* (III). A solution of sodium amyloxide (sodium 9 g., amyl alcohol 1000 c.c.) was saturated with dry hydrogen sulphide with precautions against clogging. 9 : 10-Dibromoanthracene (30 g.) was then added and the mixture heated to boiling, the stream of hydrogen sulphide being maintained throughout the whole reaction. The solution became light red and then dark brown; after 12 hours, no 9 : 10-dibromoanthracene separated on cooling. No dithioheptacyclene was thrown out of solution, as was invariably the case when the equivalent quantity of sodium hydrosulphide was employed (Heilbron and Heaton, *loc. cit.*). The cold amyl-alcoholic solution was shaken with water to remove inorganic salts, and the brown precipitate thereby produced was removed, dried, and repeatedly crystallised from benzene, dianthranyl disulphide being obtained in orange prisms, m. p. 223°. On treatment with zinc dust and glacial acetic acid,

it was readily reduced to 9-anthranyl mercaptan, m. p. 90° (Friedländer and Simon, *loc. cit.*) (Found: C, 80·1; H, 4·3; S, 15·0. Calc., C, 80·4; H, 4·3; S, 15·3%). In later experiments, it was found that the yield of dianthranyl disulphide could be considerably increased (40% calculated on the dibromoanthracene) by cutting off the current of hydrogen sulphide during the heating process. Experiments were carried out substituting 9 : 10-dichloroanthracene for the bromo-derivative, potassium for sodium, and butyl alcohol for amyl alcohol, but with none of these variations was the yield of disulphide so satisfactory.

Dianthranyl oxide (IV). The amyl-alcoholic mother-liquors from the above experiment were dried over anhydrous sodium sulphate and concentrated; the yellow substance that slowly separated from the cold solution proved extremely troublesome to crystallise, but was ultimately obtained in long, straw-coloured needles from alcohol, m. p. 213° (Found: C, 90·6; H, 5·0. $C_{28}H_{18}O$ requires C, 90·8; H, 4·9%). Dianthranyl oxide was not affected by alkalis alone, but on reduction with zinc dust and hot sodium hydroxide solution it yielded anthracene (identified as the picrate) and anthranol, m. p. 120° (not sharp) (compare Meyer, *Annalen*, 1910, **379**, 37). Like so many of these derivatives, dianthranyl oxide was not invariably obtained in all the experiments carried out and it has been impossible to ascertain the exact conditions of formation.

Treatment of 9 : 10-*Dibromoanthracene with less than one Equivalent of Sodium Hydrosulphide.*—When less than 1 equivalent of sodium (2 g. Na : 20 g. dibromoanthracene) was used under the conditions described in the first experiment, dithioheptacyclene began to separate after 6 hours; the reaction was completed after 9 hours' boiling. The product was purified as described in Part I (yield 80—90%).

Action of Sodium Sulphide.—9 : 10-Dibromoanthracene (15 g.) was added to a solution (300 c.c.) of sodium sulphide (16 g.) prepared by mixing solutions of equivalent quantities of sodium hydrosulphide and sodium amyloxide in amyl alcohol. Very little change occurred on heating at 140°, and even after 2 days' boiling the bulk of the dibromoanthracene separated on cooling. The mixture was therefore heated in an autoclave at 150° for 2 hours. On cooling, dithioheptacyclene separated in almost quantitative yield (Found: C, 80·8; H, 3·9; S, 15·2. Calc., C, 80·8; H, 3·8; S, 15·4%). Using only the equivalent quantity of sodium sulphide had very little effect, a small quantity of dianthranyl disulphide, together with anthracene and unchanged dibromoanthracene, being obtained after 3 days' boiling.

Treatment of 9 : 10-*Dibromoanthracene with Sodium Disulphide.—Dianthranyl disulphide.* A solution of sodium amyloxide (300 c.c.) containing 6 g. of sodium was converted into sodium sulphide as described above, and the theoretical quantity of powdered sulphur (4 g.) added. The mixture was gently boiled for 3 hours together with dibromoanthracene (15 g.), the colour becoming light red and finally dark brown. The solution was filtered from a small residue of unchanged 9 : 10-dibromoanthracene, the filtrate distilled to remove as much amyl alcohol as possible, and then steam-distilled. The residual light red alkaline solution contained a deep brown semi-solid mass which quickly solidified. After six crystallisations from benzene in presence of animal charcoal, orange crystals (m. p. 223°) of dianthranyl disulphide were obtained (weight of crude product : 10 g.).

By employing butyl alcohol (b. p. 116°) in place of amyl alcohol and heating for 8 hours, the whole of the dibromoanthracene was utilised and a dark red solution resulted from which the dianthranyl disulphide was completely precipitated by treatment with small quantities of water. By adopting this method, resin formation was prevented and an average yield of 60% of dianthranyl disulphide, calculated on the weight of the dibromoanthracene used, resulted (Found : C, 80·3, 80·1; H, 4·5, 4·6; S, 15·0. Calc., C, 80·4; H, 4·3; S, 15·3%).

ms-*Dibromodiheptacyclene disulphide* (VI) was obtained by heating a mixture of 9 : 10-dibromoanthracene (15 g.), crystallised sodium disulphide (5 g.), and amyl alcohol (1000 c.c.) in the autoclave for 4 hours at 200°. The yellow, amorphous product was boiled with water to remove inorganic matter and again, after drying, with xylene to remove unchanged dibromoanthracene. It was insoluble in all organic solvents and resisted reduction and the action of boiling alcoholic potash (Found : C, 72·5; H, 3·5; S, 6·7; Br, 17·4. $C_{56}H_{28}Br_2S_2$ requires C, 72·7; H, 3·0; S, 6·9; Br, 17·4%).

Dianthranyl Tetrasulphide (XI).—A sodium polysulphide mixture was prepared by slowly heating hydrated sodium sulphide ($Na_2S,9H_2O$; 60 g.) with finely powdered rock sulphur (24 g. for 2 hours at a maximum temperature of 150°. The fused orange melt was cooled and while still syrupy was added to 9 : 10-dibromoanthracene (40 g.) dissolved in amyl alcohol (700 c.c.); after being heated under reflux for 2 days, the solution was deep red. On standing over-night or longer, dianthranyl tetrasulphide separated. After boiling with water to dissolve inorganic matter, it was crystallised from benzene, separating in yellow spangles, m. p. 190° (Heilbron and Heaton, *loc. cit.*, give m. p. 194°) (yield : 33%). If the amyl alcohol is impure or if the crude polysulphide is allowed to

solidify before addition to the amyl-alcoholic solution, a quantity of free sulphur is deposited with the dianthranyl tetrasulphide, rendering purification extremely difficult. The identity of this compound with Heaton and Heilbron's dithiodianthrone disulphide (VIII) was proved by mixed melting-point determinations and by analysis (Found: C, 69·9, 69·9; H, 4·2, 4·0; S, 26·2. Calc., C, 69·7; H, 3·7; S, 26·5%).

Dianthranyl tetrasulphide was boiled with alcoholic sodium hydroxide for 3 hours, and the hot, deep red solution filtered and set aside; dianthranyl disulphide was slowly deposited. A repeat experiment was carried out, but in this case the filtrate, which was immersed in powdered ice, was acidified with dilute acetic acid; hydrogen sulphide was evolved and a buff-coloured precipitate of dianthranyl disulphide separated. That the tetrasulphide is decomposed by the alkali to give in the first place 9-anthranyl mercaptan was proved by the actual isolation of this compound from the reaction mixture in which the heating was suspended immediately the dianthranyl tetrasulphide had gone into solution. The hot solution was rapidly saturated with carbon dioxide and the residue washed with hot water to remove sodium carbonate. After drying, it separated from light petroleum in yellow crystals, m. p. 90°, which were freely soluble in dilute aqueous sodium hydroxide and readily oxidised by potassium ferricyanide solution to the disulphide.

THE UNIVERSITY, LIVERPOOL. [*Received, July 18th*, 1925.]

CCCVIII.—*The Reaction between Sodium Hypobromite and Carbamide.*

By MAXWELL BRUCE DONALD.

THE reaction between carbamide and sodium hypobromite may be represented as:

$$CON_2H_4 + 3NaOBr \longrightarrow CO_2 + N_2 + 3NaBr + 2H_2O,$$

but in actual practice it is found that it never goes to completion. The course of the reaction can be followed by estimating (1) the amount of nitrogen evolved, (2) the amount of hypobromite decomposed, or (3) the amount of carbonate formed. All these methods give substantially the same results and indicate that, with the usual methods of performing the experiment, the reaction goes only to about 90% of completion.

The incompleteness of the reaction has been attributed to various

causes, such as (1) the solubility of nitrogen in the hypobromite solution, (2) the formation of a compound of carbamide and bromous acid (Hüfner, *J. pr. Chem.*, 1871, **3**, 1), (3) the impurity of the nitrogen (Rayleigh and Ramsay, *Phil. Trans.*, 1895, **186**, *A*, 187; Rayleigh, *Proc. Roy. Soc.*, 1898, **64**, 95; Krogh, *Z. physiol. Chem.*, 1913, **84**, 379; Hurtley, *Biochem. J.*, 1921, **15**, 11), (4) the formation of oxides of nitrogen in the solution (Fauconnier, *Bull. Soc. chim.*, 1880, **33**, 102; Luther, *Z. physiol. Chem.*, 1889, **13**, 500; Krogh, *loc. cit.*). None of these explanations, however, is adequate (see, for example, Lescœur, *J. Pharm. Chim.*, 1919, **20**, 305; Werner, J., 1922, **121**, 2318; Margosches and Rose, *Biochem. Z.*, 1923, **137**, 542).

The alternative suggestion (Fenton, J., 1878, **33**, 300; P., 1895, 138; see also Lescœur, *loc. cit.*; Margosches and Rose, *loc. cit.*) that the reaction does not go to completion because of the formation of sodium cyanate is supported by the evidence brought forward in the present communication. The work of Margosches and Rose, on which the view was based that the formation of sodium cyanate cannot be the chief cause of the nitrogen deficit, is inconclusive, since no account was taken of the composition of the hypobromite used.

Experimental.

The gasometric method was found to be unsatisfactory for two reasons. The usual solution (40% brominated 10*N*-sodium hydroxide)* was made by adding bromine to a sodium hydroxide solution cooled to below 0° and analysed for hypobromite by sodium arsenite and for total hypobromite and bromate by sodium thiosulphate. The original solution was then kept for 20 hours and analysed again. Although there was no change in the thiosulphate titration, the hypobromite had been half converted into bromate over-night. The old hypobromite solution evolved about 3% more nitrogen from a carbamide solution than the freshly prepared hypobromite. This, as will be seen from subsequent results, is probably due to the decreased ratio of hypobromite to hydroxide.

The other objection to this method is that the reaction between carbamide and hypobromite gives off a considerable amount of heat; in fact, Smith (*Chem. News*, 1895, **71**, 259) used such heat as a basis for determining the amount of carbamide in urine. Wagner (*Z. anal. Chem.*, 1874, **13**, 383) suggests keeping the reaction vessel under water; but the volume of gas only becomes constant 15

* A hypobromite solution made by adding 25 c.c. of bromine (1 equiv.) to 100 g. of sodium hydroxide (2·5 equivs.) dissolved in water, and making up to 250 c.c. is described as a 40% brominated 10*N*-sodium hydroxide solution.

minutes after the reaction, even when it is kept in a well-stirred thermostat. The factor generally given in text-books for 40% brominated 10*N*-sodium hydroxide is 0·92. Careful measurements with thermostat control, using freshly prepared cool hypobromite and applying all corrections to the volume of gas evolved, gave 0·90, whereas the titration method shows that the factor should be 0·87.

More trustworthy results were obtained by estimating the hypobromite decomposed. The procedure was to add the carbamide solution slowly to the hypobromite, allow the reaction to proceed with occasional shaking for 5 minutes, dilute the reaction mixture to 500 c.c., and add about 20 c.c. of 3*N*-hydrochloric acid and a solution containing about 5 g. of potassium iodide. The solution was kept for 2 minutes and then titrated with thiosulphate, with starch as an indicator. There was a certain tendency to " reblue " on standing. The difference between the amounts of thiosulphate required for this titration and for the hypobromite alone gives the equivalent amount of hypobromite which has been used up in the reaction. The carbamide was recrystallised three times from alcohol and dried at 100°.

A number of experiments were undertaken to determine the chief factors which influenced this reaction at room temperature. Excess of hypobromite had no effect, confirming previous observations on a similar reaction with ammonia (*Analyst*, 1924, **49**, 375). The actual concentration of the hypobromite had no effect at moderate concentrations. Thus a 40% brominated 4*N*-sodium hydroxide solution was diluted in steps down to 0·25*N* without any effect on the reaction. In stronger solutions of hypobromite, there are secondary effects due to time changes in the hypobromite–hydroxide ratio to be allowed for. The chief factor at room temperature was the extent to which the sodium hydroxide had been brominated.

Some of the experimental results obtained with carbamide and various hypobromite solutions are in Table I. The expression " c.c. thio. required " indicates the difference in thiosulphate required for a blank and that required after the carbamide has been added to the hypobromite.

Similar results are obtained with hypobromite solutions prepared from sodium hydroxide as strong as 2*N*. Both titration and gasometric methods show that the nitrogen deficit becomes greater as the percentage bromination increases until the hydroxide is 75% brominated. At this point a sudden change occurs, the amount of gas evolved still decreases, but a slow oxidation sets in. After 30 minutes, an amount of hypobromite is used up which is about equivalent to the

TABLE I.

Sodium thiosulphate 0·1963*N*. Sodium hydroxide 0·496*N*. 5 C.c. of carbamide solution contain 0·075 g., which is equivalent to 38·3 c.c. of thiosulphate.

No. of sol.	% Brominated.	C.c. of thio. required after 5 mins.	15 mins.	30 mins.	Carbamide decomposed %.
1	15	34·2	—	—	89·3
2	30	33·8	—	—	88·4
3	45	33·1	—	—	86·4
4	60	31·0	31·1	30·9	81·0
5	75	29·7	29·1	29·4	77·6
6	80	29·2	37·5	38·7	
7	85	33·5	38·6	37·8	
8	90	35·1	37·7	38·7	
9	95	36·5	37·9	38·5	
10	97·5	—	4·2	4·0	

quantity of carbamide taken (*i.e.*, 38·3 c.c. of thio.). When the sodium hydroxide is completely brominated, there is no gas evolution and no hypobromite is used up.

Sodium cyanate was prepared by the method of Leuchs and Geserick (*Ber.*, 1908, **41**, 4171) from urethane and sodium in boiling benzene and was twice recrystallised from pure alcohol. With it and with the same hypobromite solutions as before, the following results were obtained.

TABLE II.

5 C.c. of sodium cyanate taken contain 0·075 g., equiv. to 17·7 c.c. of 0·196*N*-thio.

No. of solution.	% Bromination.	C.c. of thio. after 5 mins.	15 mins.
5	75	—	—
6	80	0·4	0·3
7	85	0·4	0·3
8	90	1·0	0·7
9	95	17·9	18·0

There is no action of hypobromite on sodium cyanate below the composition 75% brominated. Above this value the hypobromite reacts slowly with the sodium cyanate, but with 100% brominated solutions there is a vigorous gas evolution from the mixture.

The figures for sodium cyanate (Nos. 7 and 8) do not show complete oxidation, as would be expected from the figures in Table I. Another series of experiments was therefore made with the same hypobromite solutions, using a mixture of carbamide and sodium cyanate.

These figures point to the fact that the deficit of nitrogen is due to the formation of sodium cyanate and that with hypobromite solutions brominated to more than 75% and less than 95% a secondary oxidation of the sodium cyanate is induced only if carbamide is present. They also show that the rate of this secondary oxidation

TABLE III.

5 C.c. of the solution contain 0·0375 g. each of carbamide and sodium cyanate, which are equivalent to 19·15 and 17·7 c.c. of 0·196*N*-thiosulphate respectively.

No. of solution.	% Bromination.	C.c. of thio. required after 5 mins.	15 mins.
4	60	16·2	16·1 carbamide alone
7	85	15·8	28·5
8	90	28·2	28·4

is greater with increase in the amount of bromination of the sodium hydroxide. Carbamide is not acted upon by 100% sodium hypobromite, as there is no excess of sodium hydroxide to decompose the compound which it probably forms with the bromine.

The potential of a platinum electrode dipping into the various solutions shows that there is no marked change in the oxidising power except in the neighbourhood of completely brominated solutions.

TABLE IV.

No. of solution.....	1	3	5	7	9	10
E.M.F. volt	+0·756	0·790	0·810	0·830	0·850	0·981

Summary.

The chief factor influencing the deficit of nitrogen in the reaction between carbamide and sodium hypobromite at room temperature is the extent to which the sodium hydroxide has been brominated. The effect of this variable has been studied for all brominations from 0 to 100%. The reaction does not go to completion owing to the formation of sodium cyanate. The amount of sodium cyanate formed becomes greater as the ratio of hypobromite to hydroxide increases until it corresponds to 75% bromination, when it is oxidised in a secondary reaction. Sodium cyanate solutions are not appreciably oxidised by 75 to 90% hypobromite solutions except in the presence of carbamide. With pure hypobromite (*i.e.*, without any excess of sodium hydroxide present) sodium cyanate solutions are vigorously decomposed. The experiments of Margosches and Rose proving that sodium cyanate is not formed in the reaction are inconclusive, since they do not take into account the effect of the composition of the hypobromite. The use of 10*N*-sodium hydroxide solutions for the estimation of carbamide gasometrically leads to inaccurate results.

The author wishes to thank Professor J. C. Philip, F.R.S., for his kind advice and interest in this research.

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SOUTH KENSINGTON. [*Received, May 16th,* 1925.]

CCCIX.—*Nitrosation of Phenols. Part II. Nitrosation of 3-Bromo-, 2-Bromo-, 3-Iodo-, and 2-Iodo-phenol. Evidence for the Nitroso-formula of 4-Nitrosophenol.*

By HERBERT HENRY HODGSON and FRANCIS HARRY MOORE.

THE investigation now to be described, dealing mainly with the nitrosation of 3-bromo- and 3-iodo-phenol, supplements work on 3-chlorophenol (J., 1923, **123**, 2499).

Unlike 3-chloro-4-nitrosophenol, 3-bromo-4-nitrosophenol is so sensitive to transformation that the quinoneoxime form is produced in every solvent except ether. 3-Iodo-4-nitrosophenol has been obtained only in the quinoneoxime modifications. Geometrical isomerides of both compounds have been isolated which exhibit differences in colour (see also Kehrmann and Wolff, *Ber.*, 1900, **33**, 1539; Kehrmann and Denk, *ibid.*, p. 3297). Oxidation to the corresponding halogenated nitrophenols has established the 4-positions of the nitroso-groups, and molecular-weight determinations the unimolecular character of the isomerides.

2-Chloro- and 2-bromo-4-nitrosophenol were readily obtained by the general process for nitrosating *m*-halogenated phenols (*loc. cit.*); but from 2-iodophenol a tar was produced, and the nitroso-compound was obtained only by working at great dilution and in the presence of acetic instead of sulphuric acid. These three nitroso-compounds could not be converted into the quinoneoxime forms, the immobility of the phenolic hydrogen in proximity to a halogen atom being thus made manifest.

A very fine specimen of nitrosophenol free from resinous matter has been prepared from phenol by the general nitrosation method; it melts at 133°, *i.e.*, 7° higher than the m. p. (126°) usually recorded. A specimen prepared 2 years ago is still in good condition.

The data in the following table are claimed to support the view that 4-nitrosophenol is a genuine nitroso-compound and not a quinoneoxime.

Substance.	M. p. of nitroso-compound.	M. p. of quinoneoximes.
Phenol	133° (126° recorded)	126° (prepared from benzoquinone)
2-Chlorophenol	148° with decomp.	—
2-Bromophenol	150° „ „	—
2-Iodophenol	Decomp. 152°	—
3-Chlorophenol	135° with decomp.	172° and 178°
3-Bromophenol	139° „ „	189° and 190°
3-Iodophenol	—	Decomp. 185—195°
2:5-Dichlorophenol	146°	Decomp. 155—160°
ψ-Cuminol *	134° (4-nitroso-2:3:5-trimethylphenol)	184°

* Nietzki and Schneider, *Ber.*, 1894, **27**, 1426.

Experimental.

Nitrosation of 3-*Bromo-*, 2-*Bromo-*, *and* 3-*Iodo-phenol.*—The method for preparing 3-chloro-4-nitrosophenol (J., 1923, **123**, 2502) was found generally applicable; the nitroso-compounds, however, formed gradually and separated, partly as pale yellow crystals (0·5—1 g.) and partly as tars, from which, after draining and washing with cold benzene, about 2 g. more of the products were obtained.

3-*Bromo*-4-*nitrosophenol* dissolves readily in alcohol or ether and is moderately easily soluble in hot benzene or light petroleum, but almost insoluble in the cold solvent. It was obtained in yellow needles, m. p. 139° (decomp.), by addition of light petroleum to an ethereal solution (Found: Br, 39·5; N, 7·0. $C_6H_4O_2NBr$ requires Br, 39·6; N, 6·9%).

3-*Bromo*-p-*benzoquinone*-4-*oxime* was obtained in red needles when the preceding compound was crystallised from benzene, dilute hydrochloric acid, and dilute alcohol; the three products melted and decomposed at 187°, 188°, and 186°. On recrystallisation from dilute hydrochloric acid, the quinoneoxime was obtained in orange needles, m. p. 188° (decomp.) (Found: Br, 39·6; N, 7·1; *M*, cryoscopic in phenol, 189. $C_6H_4O_2NBr$ requires Br, 39·6; N, 6·9%; *M*, 202). All the solvents tried except cold ether effected the conversion.

Action of Alkalis on 3-*Bromo*-4-*nitrosophenol.*—The nitroso-compound dissolves in aqueous sodium hydroxide (10%) to a red solution which froths after a few seconds. If the solution is acidified immediately, a pale yellow almost colourless substance of m. p. 189—190° (needles from benzene) is precipitated (Found: Br, 39·55; N, 7·2), but if it is kept for some time a dark-coloured substance of indefinite m. p. is produced on acidification. Sodium carbonate effects the same transformation unaccompanied by frothing, or decomposition on short standing.

Interconversion of the Geometrical Isomerides.—Dissolution of the orange form of the quinoneoxime in alkalis (unaccompanied by frothing), followed by acidification in the cold, produces the colourless form, and crystallisation of the latter from dilute hydrochloric acid converts it into the orange isomeride.

Liebermann's Nitroso-reaction.—All three products gave identical results owing to the ready conversion of two of them into the acid-stable form. To 0·05 g. of each isomeride, 0·1 g. of phenol and 1 c.c. of concentrated sulphuric acid were added. The solutions were deep green and became brownish-red on dilution and then violet on addition of sodium hydroxide.

Oxidation of 3-*Bromo*-4-*nitrosophenol and its Tautomerides to* 3-*Bromo*-4-*nitrophenol.*—Oxidation proceeds much more readily than in the case of 3-chloro-4-nitrosophenol. A solution of 0·5 g. of any one of the three isomerides in water (100 c.c.) containing potassium ferricyanide (5 g.) and sodium hydroxide (5 g.) was kept for 48 hours at room temperature and then acidified with dilute sulphuric acid (25%). The solution was filtered, shaken with ether, the solvent removed from the extract, the residue treated with a minimum of aqueous sodium hydroxide (10%), and the alkaline solution acidified in the cold with concentrated hydrochloric acid; the brown precipitate thus obtained crystallised from benzene in almost colourless needles, m. p. 131° (Auwers and Deines, *loc. cit.*, give m. p. 130—131°) (Found: Br, 36·75; N, 6·5. Calc. for $C_6H_4O_3NBr$, Br, 36·7; N, 6·4%).

2-*Bromo*-4-*nitrosophenol.*—This nitroso-compound is not transformed into a quinoneoxime by hot dilute mineral acids. It crystallises from benzene in light brown needles and from dilute alcohol in red needles, m. p. 150° (Found: Br, 39·4; N, 7·0. $C_6H_4O_2NBr$ requires Br, 39·6; N, 6·9%). The colour produced in the Liebermann nitroso-reaction is deep green and changes to wine-red on dilution; it reverts to deep green in aqueous sodium hydroxide. Oxidation with ferricyanide as described above converts the nitroso-compound into 2-bromo-4-nitrophenol, m. p. 112° (Found: Br, 36·6; N, 6·5. Calc., Br, 36·7; N, 6·4%).

3-*Iodo*-p-*benzoquinone*-4-*oxime.*—The nitrosation product of 3-iodophenol has no m. p.; it darkens at 170—180°, begins to decompose at 185°, and a deep reddish-brown vapour is evolved at 200°. The compound is readily soluble in alcohol or ether, moderately easily soluble in hot benzene but very sparingly soluble in the cold solvent, and insoluble in light petroleum. The yellow needles obtained from its solution in benzene or hot dilute hydrochloric acid decompose at 185—195°; if the latter solution is boiled for a few minutes, iodine is liberated and no crystallisation ensues. Light petroleum added to an ethereal solution of the quinoneoxime produces small, deep yellow prisms. This isomeride, which is tentatively assumed to be the *syn*-form (compare J., 1923, **123**, 2499), has a normal molecular weight in phenol solution (Found: N, 5·8; I, 50·9; *M*, cryoscopic in phenol, 254. $C_6H_4O_2NI$ requires N, 5·6; I, 51·0%; *M*, 249).

The *syn*-modification dissolves in 10% aqueous sodium hydroxide without frothing. From the red solution, on acidification, a very pale straw-coloured substance is precipitated. This, the *anti*-form, decomposes at about 185° and is highly dissociated in phenol solution (Found: N, 5·7; I, 50·9%; *M*, cryoscopic in phenol, 160).

The Liebermann reaction produced a yellowish-brown colour, which changed to reddish-brown when the solution was diluted or made alkaline. Decomposition appears to have taken place.

Oxidation with alkaline ferricyanide as described above gave *3-iodo-4-nitrophenol*, which crystallised from alcohol in long, slender, almost colourless needles, m. p. 123° (Found: N, 5·5. $C_6H_4O_3NI$ requires N, 5·3%), and was identified by comparison with a specimen prepared by nitrating 3-iodophenol.

Preparation of 2-Iodophenol.—2-Iodonitrobenzene was obtained in 91% yield from *o*-nitroaniline by the usual procedure; only a slight excess of potassium iodide, however, was employed. It melted at 50—51° (Nölting and Wrzesinski, *Ber.*, 1875, **8**, 820, give m. p. 43°). Its reduction with tin and hydrochloric acid produced a mixture of 2-iodo- and 2-chloro-aniline, and the yield of the former obtained by means of ferrous sulphate and ammonia was poor (compare Körner and Wender, *Gazzetta*, 1887, **17**, 486). 2-Iodonitrobenzene (28 g.), iron filings (28 g.), glacial acetic acid (70 c.c.), and water (70 c.c.) were mixed together and the mild reaction was completed by heating on the water-bath. The product was made alkaline with sodium bicarbonate and distilled with steam. The 2-iodoaniline thus obtained (22 g. or 89·5%; m. p. 57°. Körner and Wender, *loc. cit.*, give m. p. 56·5°) was converted, by rapidly cooling a hot solution in concentrated sulphuric acid (20 c.c.) and water (50 c.c.), into small crystals of the sulphate, which was diazotised and the excess of nitrous acid destroyed by carbamide; the diazo-solution was added drop by drop to a boiling solution of sulphuric acid (50 c.c.) and water (50 c.c.) through which a current of steam was passing. The 2-iodophenol thus obtained (yield 20 g. or 91%) melted at 40° after crystallisation from ether (Schall, *Ber.*, 1883, **16**, 1897; 1887, **20**, 3363, gives m. p. 39—40°).

Nitrosation of 2-Iodophenol.—The general method was useless in this case, tarry matter only being formed. The main product of the action of amyl nitrite and glacial acetic acid on 2-iodophenol in benzene solution was 2-iodo-6-nitrophenol, which was isolated by means of its volatility in steam. This compound, which was also prepared by nitrating 2-iodophenol, crystallised from light petroleum in bright yellow, feathery needles, m. p. 109°, and formed a red sodium salt.

A solution of 2-iodophenol (4 g.) and sodium nitrite (7 g.) in water (850 c.c.) was cooled to 10° and treated gradually with a mixture of glacial acetic acid (4·5 c.c.) and water (5 c.c.). After 24 hours, the solution was filtered, and shaken with ether. The extract was treated with 10% sodium hydroxide, and the deep-

coloured aqueous layer very cautiously acidified in the cold. The yellow precipitate (1 g.) of 2-*iodo*-4-*nitrosophenol* crystallised from benzene or dilute hydrochloric acid in yellow needles, which decomposed at 152°. No conversion into a quinoneoxime could be effected (Found: N, 5·7; I, 50·85; *M*, cryoscopic in phenol, 255. $C_6H_4O_2NI$ requires N, 5·6; I, 51·0%; *M*, 249). The colour produced in the Liebermann reaction was deep green; it changed to crimson on dilution and to blue when the solution was made alkaline. 2-Iodo-4-nitrophenol, m. p. 86—87°, was obtained by oxidising 2-iodo-4-nitrosophenol with ferricyanide and by nitrating 2-iodophenol (Found: N, 5·4. Calc., N, 5·3%).

The authors desire to thank the British Dyestuffs Corporation for gifts of the chemicals used in this investigation.

THE TECHNICAL COLLEGE,
HUDDERSFIELD. [*Received, April 9th,* 1925.]

CCCX.—*Nitration of Phthal- and Succin-*p*-tolil.*

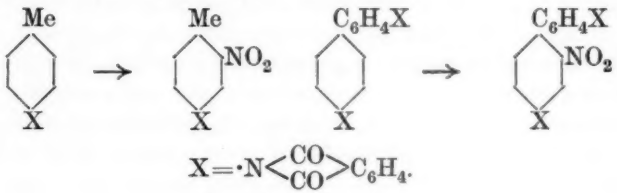
By OSCAR L. BRADY, WILLIAM G. E. QUICK, and WALTER F. WELLING.

THE nitration of aniline in the presence of a large quantity of concentrated sulphuric acid has long been known to give *m*-nitroaniline (Hübner and Frericks, *Annalen*, 1881, **208**, 299; Noelting and Collin, *Ber.*, 1884, **17**, 261; Bruns, *Ber.*, 1895, **28**, 1954; Tingle and Blanck, *Amer. Chem. J.*, 1906, **36**, 605), and of *p*-toluidine to give 2-nitro-*p*-toluidine. Acylated amines, however, on nitration usually give compounds in which the nitro-group has entered in the *o*- or *p*-position to the acylamino-group, but in some cases, if a large quantity of concentrated sulphuric acid is present, meta-substitution occurs; for example, under these conditions Noelting and Collin (*loc. cit.*) obtained after hydrolysis a small quantity of *m*-nitroaniline from acetanilide and a considerable quantity of 2-nitro-*p*-toluidine from aceto-*p*-toluidide; with plain nitric acid, however, the group entered in the ortho- or para-position to the acylamino-group. Phthal-*p*-tolil on nitration with a mixture of sulphuric and nitric acids gives mainly 2-nitro-*p*-toluidine (D.R.-P. 141893).

Sulphuric acid was employed in all these nitrations, but Miolati and Lotti (*Gazzetta*, 1897, **27**, i, 298) obtained 2-nitro-*p*-toluidine by nitrating succin-*p*-tolil with fuming nitric acid. (Compare also Cain and Micklethwait, *J. Chem. Soc.*, 1914, **105**, 1442, for the nitration of diphthalyltolidide.) This problem has now been investigated on more quantitative lines, the succinyl-, phthalyl-,

3-nitrophthalyl-, and tetrachlorophthalyl-compounds being nitrated with fuming nitric acid alone. Under these conditions, the aniline derivatives gave almost exclusively *p*-nitroaniline, but the derivatives of *p*-toluidine all gave 2-nitro-*p*-toluidine as the main product. It appears, therefore, that the dibasic acyl group does not sufficiently influence the amino-group to enable meta-substitution to occur, but so reduces its directive influence in the case of *p*-toluidine as to enable the comparatively feebly directive methyl group to take control. Nitrophthal-, tetrachlorophthal-, and succin-*p*-tolil gave approximately 84%, and phthal-*p*-tolil 76%, of 2-nitro-*p*-toluidine; the nature of the dibasic acid accordingly does not greatly influence the proportion of the isomerides formed.

This investigation arose from the study of the isomerism of the dinitrobenzidines (compare Brady and McHugh, J., 1923, **123**, 2047, where the literature of these compounds is summarised) and the behaviour of phthal-*p*-tolil in giving 2-nitro-*p*-toluidine with fuming nitric acid is consistent with the possibility that one of the nitro-groups in Bandrowski's dinitrobenzidine, obtained by the nitration of phthalylbenzidine, is in the meta-position to the amino-group, since one phthalylaminophenyl group can be regarded as replacing methyl in phthal-*p*-tolil.



$$X = \cdot N\!<\!\begin{matrix}CO\\CO\end{matrix}\!>\!C_6H_4.$$

EXPERIMENTAL.

The System 2-*Nitro*-p-*toluidine*–3-*Nitro*-p-*toluidine*.—The fusion diagram was constructed in the usual way from cooling curves of mixtures of the pure compounds. The results are in Table I. In the neighbourhood of the eutectic, crystallisation was very slow and the freezing point was easily missed if the rate of cooling exceeded 0·3° per minute; indeed with two mixtures no definite arrest was obtained until the eutectic temperature was reached, the freezing point being indicated only by the change of slope of the cooling curve; these values are given in brackets.

Nitration of Phthal-p-*tolil*.—Two parts of *p*-toluidine were heated with one of phthalic anhydride for 2 hours on the water-bath. The product was extracted repeatedly with hot alcohol, and the sparingly soluble residue crystallised from benzene. The phthalyl compound so obtained was added in small portions to 10 times its

TABLE I.

% 3-Nitro-*p*-toluidine.	F. p.	% 3-Nitro-*p*-toluidine.	F. p.	Eutectic.
0	74·8°	33·1	(60·9°)	56·1°
10·5	69·0	38·7	(65·6)	56·2
18·0	64·1	49·7	74·0	
23·5	60·3	55·0	78·4	
29·0	56·3	100	116·7	

weight of nitric acid (*d* 1·5) cooled in ice, the mixture kept on ice for 10 minutes and then poured on to crushed ice. When the ice had melted, the solid was collected, washed free from nitric acid, and hydrolysed by boiling with 2*N*-sodium hydroxide for 2 hours. After cooling, the mixture of nitrotoluidines which separated was collected, washed with water, and dried thoroughly in a vacuum over concentrated sulphuric acid. The freezing point was 59·9°, corresponding to 76% or 67% of 2-nitro-*p*-toluidine; the former value was shown to be correct by obtaining the right rise in freezing point by the addition of a known amount of pure 2-nitro-*p*-toluidine. The eutectic of the nitration mixture separated at 55·1° as against 56·2° for the synthetic mixture, indicating the presence of a small quantity of one or more other compounds, possibly 2 : 3-, 2 : 5-, 2 : 6-, and 3 : 5-dinitro-*p*-toluidines, all of which might be formed in the nitration; the amount, however, must be small and cannot greatly influence the relative proportions of the 2- and 3-nitro-*p*-toluidines here given. The separation of the main constituents of the hydrolysis product was achieved by acetylating with acetic anhydride with the addition of a drop of concentrated sulphuric acid, pouring into water, and crystallising the product three times from 50% alcohol, when pure 2-nitroaceto-*p*-toluidide was obtained. The mother-liquors from the crystallisation were hydrolysed by boiling with 2*N*-sodium hydroxide, and the amine was crystallised three times from 50% alcohol, when a small quantity of pure 3-nitro-*p*-toluidine was obtained. The crude phthalyl compound on crystallisation from benzene yielded pure phthal-2-nitro-*p*-tolil (D.R.-P. 141893).

Nitration of Succin-p-tolil.—Succin-*p*-tolil, prepared in an analogous way to the phthalyl derivative by means of succinic anhydride and heating to 150°, was nitrated in a manner similar to the above. The yield of mixed amines was poor; the product froze at 65·2°, corresponding to 84% of 2-nitro-*p*-toluidine.

Phthal-2-nitro-p-toluidic and Succin-2-nitro-p-toluidic Acids.—When phthal-2-nitro-*p*-tolil was warmed with 2*N*-sodium hydroxide, it dissolved completely; hydrochloric acid then precipitated the toluidic acid. This was purified by dissolving in cold dilute ammonia,

filtering off any amine, reprecipitating with hydrochloric acid, and crystallising from dilute alcohol, when *phthal*-2-*nitro*-p-*toluidic acid* was obtained as a cream-coloured, crystalline powder melting and decomposing indefinitely at about 160° (Found : N, 9·4. $C_{15}H_{12}O_5N_2$ requires N, 9·3%). The succintoluidic acid underwent further hydrolysis with ease, and in its preparation in an analogous manner to the above the alkali must not be warmed above 50° and solution must be obtained as rapidly as possible by vigorous shaking. After purifying by solution in ammonia and reprecipitation, it was dried and crystallised from benzene to which a few drops of alcohol had been added. *Succin*-2-*nitro*-p-*toluidic acid* crystallises in almost colourless, feathery needles, m. p. 163° (Found : N, 11·3. $C_{11}H_{12}O_5N_2$ requires N, 11·1%).

Nitration of 3-*Nitrophthal*-p-*tolil*.—A mixture of *p*-toluidine (30 g.) and nitrophthalic anhydride (25 g.) was heated for an hour at 130° with stirring. After cooling, the mass was dissolved in acetone, reprecipitated by the cautious addition of water, and the product crystallised from alcohol, when 3-*nitrophthal*-p-*tolil* was obtained as a yellow powder, m. p. 149° (Found : N, 9·8. $C_{15}H_{10}O_4N_2$ requires N, 9·9%). This was nitrated and hydrolysed as above, and the amines were extracted from the alkaline solution with ether. After drying in a vacuum, they froze at 64·7° (a repetition of the whole of the operations gave 64·5°), corresponding to 83·5% of 2-nitro-*p*-toluidine. The eutectic froze at 54·8°. The yield of amine from the nitrated product was small owing apparently to partial decomposition by the alkali, but other agents such as concentrated hydrochloric acid or 50% sulphuric acid did not bring about hydrolysis.

Nitration of Tetrachlorophthal-p-*tolil*.—Tetrachlorophthal-*p*-tolil prepared in a similar way to the nitrophthalyl compound consists of a pale yellow, crystalline powder, m. p. 145° (Found : Cl, 37·4. $C_{15}H_7O_2NCl_4$ requires Cl, 37·8%). Nitration and hydrolysis were carried out as with the nitrophthalyl compound, the yield of amines being small. The freezing point of the product was 65·1°, corresponding to 84·5% of 2-nitro-*p*-toluidine.

Nitration of Succinanil and Phthalanil.—These compounds were nitrated under identical conditions with the above. From the hydrolysed product pure *p*-nitroaniline was obtained by one crystallisation; the mother-liquor from this crystallisation was investigated, but no *m*-nitroaniline could be obtained by fractional crystallisation of the amine or of its acetyl derivative.

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CCCXI.—*Substitution in Vicinal Trisubstituted Benzene Derivatives. Part III.*

By LEON RUBENSTEIN.

THE mixture of 5- and 6-nitro-3-methoxy-2-ethoxybenzaldehydes produced by nitrating 3-methoxy-2-ethoxybenzaldehyde (Davies and Rubenstein, J., 1923, **123**, 2839) has now been separated into its constituents by the method employed by Perkin, Robinson, and Stoyle to separate the isomerides formed in the nitration of *o*-veratraldehyde (J., 1924, **125**, 2355); it contains 60% of the 5-nitro- and 40% of the 6-nitro-compound.

The same method was applied in an attempt to separate the mixture of 5- and 6-nitro-2 : 3-diethoxybenzaldehydes obtained in the nitration of 2 : 3-diethoxybenzaldehyde (Davies and Rubenstein, *loc. cit.*); these were condensed with *p*-toluidine and with *m*-nitroaniline, but in neither case could a complete separation of the Schiff bases be effected by fractional crystallisation.

Evidence was obtained, however, that both in the nitration of 3-methoxy-2-ethoxybenzaldehyde and of 2 : 3-diethoxybenzaldehyde the 4-nitro-aldehyde is formed in small quantity.

EXPERIMENTAL.

Nitration of 3-Methoxy-2-ethoxybenzaldehyde and Separation of the Products.—The following modified method of nitration (compare *loc. cit.*) renders the subsequent separation easier: 3-Methoxy-2-ethoxybenzaldehyde (12 g.) cooled to 0° is added drop by drop with vigorous stirring to nitric acid (30 c.c.; *d* 1·42), the temperature being maintained at 0°. The crystals of 5-nitro-3-methoxy-2-ethoxybenzaldehyde (7·4 g.) that separate after several hours are removed. The filtrate, on dilution with water, deposits a yellowish-white mixture of 5- and 6-nitro-3-methoxy-2-ethoxybenzaldehydes, which is collected and dried. This mixture (7·4 g.) is heated with *p*-toluidine (3·6 g.) on the steam-bath during 30 minutes, and alcohol is added until a boiling solution is obtained. 5-Nitro-3-methoxy-2-ethoxybenzylidene-*p*-toluidine separates on cooling, and the 6-nitro-isomeride from the filtrate after concentration. These substances can be almost completely separated by careful fractional crystallisation from alcohol.

5-Nitro-3-methoxy-2-ethoxybenzylidene-p-*toluidine* crystallises in pale yellow, slender needles, m. p. 148° (Found: N, 9·1. $C_{17}H_{18}O_4N_2$ requires N, 8·9%). It is readily hydrolysed by hot dilute hydrochloric acid, giving 5-nitro-3-methoxy-2-ethoxybenzaldehyde, m. p. 137°. *6-Nitro-3-methoxy-2-ethoxybenzylidene*-p-*toluidine* crystallises in golden prisms, m. p. 88° (Found: N, 9·0%).

6-*Nitro*-3-*methoxy*-2-*ethoxybenzaldehyde*, readily obtained by hydrolysing the pure *p*-toluidine derivative with hot dilute hydrochloric acid, crystallises from aqueous alcohol in colourless, slender prisms, m. p. 57° (Found : N, 6·4. $C_{10}H_{11}O_6N$ requires N, 6·2%); the p-*nitrophenylhydrazone* consists of stout, brown needles, m. p. 188—189°. Treatment with acetone and alkali gives an indigotin derivative.

6-*Nitro*-3-*methoxy*-2-*ethoxybenzoic Acid*.—A mixture of the aldehyde (1 g.), water (10 c.c.), and potassium bicarbonate (0·6 g.) is boiled during the addition of hot 10% potassium permanganate solution (10 c.c.). The filtered, cooled solution is separated from a little unchanged aldehyde and acidified with hydrochloric acid. The 6-*nitro*-3-*methoxy*-2-*ethoxybenzoic acid* thus precipitated melts at 119—120° after crystallisation from hot water, in which it is fairly soluble (yield 50%) (Equiv., 240. $C_{10}H_{11}O_6N$ requires equiv., 241).

Nitration of 2 : 3-*Diethoxybenzaldehyde*.—This was carried out similarly to the nitration of 3-methoxy-2-ethoxybenzaldehyde. The material obtained (5·7 g.) was treated with *p*-toluidine (2·5 g.), and the product with alcohol, as described above; 5-*nitro*-2 : 3-*diethoxybenzylidene*-p-*toluidine* (2·4 g.) crystallised in long, slender, cream needles, m. p. 105—106° (Found : N, 8·6. $C_{18}H_{20}O_4N_2$ requires N, 8·5%); further fractionation yielded a small quantity of a substance, m. p. 100° (Found : N, 8·7%).

5-*Nitro*-2 : 3-*diethoxybenzaldehyde*, which is readily obtained by hydrolysing the pure *p*-toluidine derivative, m. p. 105—106°, with hot dilute hydrochloric acid and recrystallising the product from aqueous alcohol, consists of white needles, m. p. 71°. It does not yield an indigotin derivative with acetone and alkali and gives no depression of m. p. when mixed with a sample of 5-nitro-2 : 3-diethoxybenzaldehyde obtained by nitrating 2-hydroxy-3-ethoxybenzaldehyde and methylating the product.

6-*Nitro*-2 : 3-*diethoxybenzaldehyde*, similarly obtained from the compound, m. p. 100°, crystallises from dilute alcohol in almost colourless needles, m. p. 75—76° (Found : N, 6·0. $C_{11}H_{13}O_5N$ requires N, 5·8%). It turns green on exposure to the air, as do its solutions in all solvents. With acetone and alkali an indigotin derivative is obtained. The p-*nitrophenylhydrazone* consists of bright yellow, stout needles, m. p. 268—270°.

The author is indebted to the Research Fund Committee of the Chemical Society which has defrayed some of the expenses of this investigation.

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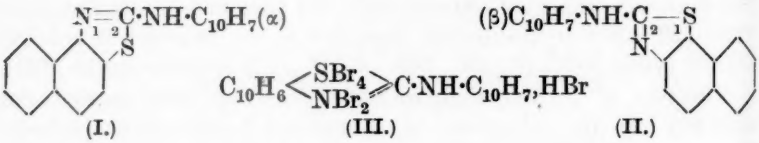
[*Received, August 14th*, 1925.]

CCCXII.—*Aminobenzthiazoles. Part II. Naphthylaminonaphthathiazole Derivatives.*

By Robert Fergus Hunter.

The curious observations on the conversion of symmetrical diarylthiocarbamides into arylaminobenzthiazole bromides recorded in Part I (this vol., p. 2023) made it of interest to extend the investigation to the halogen derivatives of the naphthalene homologues of 1-anilinobenzthiazole (I and II), and the bromination of the *s*-dinaphthylthiocarbamides in chloroform was therefore studied.



(I.) (III.) (II.)

Under conditions analogous to those employed in the previous cases (*loc. cit.*), *s*-di-α-naphthylthiocarbamide readily passed into the *tetrabromo*-addition compound of 2-α-naphthylamino-β-naphthathiazole (I), a substance having properties analogous to those of the tetrabromides described in Part I. On exposure to air it rapidly lost bromine, yielding a yellowish-orange *tribromide*; this, however, was not so stable as the tribromides of the benzenoid series, since it gradually lost bromine on exposure to the atmosphere. On treatment with sulphurous acid, the tetrabromide was rapidly reduced, the added bromine being eliminated as hydrogen bromide, and the free *base* (I) formed. The tetrabromide was converted by boiling hydroxylic solvents and alkalis into a *dibromo*-substitution derivative of the usual type (*loc. cit.*). The tetrabromide differs from those of the benzenoid series in that it is capable of uniting with hydrogen bromide and more bromine, yielding a *heptabromide*, which no doubt has the constitution (III), analogous to that of the *m*-toluthiazole heptabromide (*loc. cit.*).

On one occasion, when bromine was added to a warm suspension of di-α-naphthylthiocarbamide in chloroform, a bright red, unstable tribromo-addition compound was isolated, which was probably the hydrobromide of a dibromo-addition compound.

Since the bromination of *s*-di-α-naphthylthiocarbamide yielded as many as three bromo-addition compounds and was complicated by the tendency of the nascent thiazole to add on hydrogen bromide as well as bromine, the bromination of the naphthathiazole base itself was examined; as might have been anticipated, in

presence of excess of halogen it yielded a well-defined *hexabromide* the most probable constitution of which is

$$C_{10}H_6<\begin{matrix}SBr_4\\NBr_2\end{matrix}>C\cdot NHC_{10}H_7.$$

This compound has the usual properties of losing bromine on exposure to air, being reduced by sulphurous acid, and passing into the substitution product in presence of hydroxylic solvents and alkalis.

On bromination under similar conditions to those used in the case of the α-compound, *s*-di-β-naphthylthiocarbamide readily yielded a dark purplish-red *hexabromide* of (II), which doubtless is similar to the α-hexabromide in constitution. The β-hexabromide was isolated in two forms having identical chemical properties but different melting points. It differs from the higher bromo-addition compounds of the arylaminobenzthiazole series in being remarkably stable to air, in this respect resembling dehydrothio-toluidine dibromide (this vol., p. 1318); unlike this, however, it is decomposed by dilute alkalis and hydroxylic solvents. On treatment with sulphurous acid, the six bromine atoms are eliminated in the usual way with the liberation of (II). The direct elimination of bromine by treatment with hydroxylic solvents and alkalis had previously been observed in the case of 1 : 1-bisbenzthiazole tetrabromide (this vol., p. 1319), but this is a highly unstable substance which completely loses the whole of its added bromine on exposure to the air for some hours.

A *tribromo*-addition compound of 2-β-naphthylamino-α-naphthathiazole was also isolated, which resembled the hexabromide in its remarkable stability to air; on treatment with hydroxylic solvents and alkalis, however, the added bromine was eliminated (initially) as sodium hypobromite, with liberation of the thiazole base (II). The tribromide was reduced in the usual way by sulphurous acid, being no doubt the hydrobromide of the dibromo-addition compound of the thiazole.

The bromination of 2-β-naphthylamino-α-naphthathiazole in chloroform yielded, as might have been anticipated, the hexabromo-addition compound.

The bromine addition compounds of β-naphthylamino-α-naphthathiazole therefore differ from those of α-naphthylamino-β-naphthathiazole and of the arylaminobenzthiazoles (1) in their stability in air, which is of the order of that of dehydrothiotoluidine dibromide, (2) in losing their added halogen as hypobromite, with regeneration of the α-thiazole base, on treatment with hydroxylic solvents and alkalis, and (3) in being incapable of conversion into a stable, yellowish-orange tribromide by atmospheric oxidation.

EXPERIMENTAL.

s-Di-α-naphthylthiocarbamide was prepared from α-naphthylamine by the usual method (Hofmann, *Annalen*, 1846, **57**, 256). The crude product, after treatment with dilute acid, water, etc., was digested with boiling acetic acid and with boiling alcohol; the microcrystalline powder thus obtained had m. p. 196°; a further quantity slowly separated in prisms from the acetic acid filtrate.

2-α-*Naphthylamino*-β-*naphthathiazole Tetrabromide.* — Di-α-naphthylthiocarbamide (2 g.) was suspended in 20 c.c. of chloroform, and 2 c.c. of bromine were slowly added with continuous shaking; heat and hydrogen bromide were evolved towards the end of the bromination. The solution was refluxed for 2 minutes on a steam-bath and cooled in a freezing mixture; the *tetrabromide* then separated in minute, brilliant vermilion crystals, which were dried in a vacuum over potassium hydroxide. The tetrabromide lightened in colour at 190°, became yellow at 200°, and colourless at 260° (Found: Br, 50·2. $C_{21}H_{14}N_2Br_4S$ requires Br, 49·6%).

On exposure to air the tetrabromide lost bromine, yielding a yellowish-orange, crystalline mass of the *tribromide*, which after boiling with chloroform and drying in a vacuum was obtained in small, yellow prisms; these became pale at 200° and colourless at 280°. [Found: Br, 42·6. $(C_{21}H_{14}N_2Br_3S)_2$ requires Br, 42·4%]. On treatment with sulphurous acid, the tribromide yielded the thiazole base in the usual way.

2-α-*Naphthylamino*-β-*naphthathiazole Heptabromide.*—By using 1 g. of *s*-di-α-naphthylthiocarbamide, 6 c.c. of chloroform, and 1 c.c. of bromine diluted with a little chloroform, and proceeding as in the previous bromination, bright red granules of a *heptabromide* (III) were obtained which lost bromine and became yellow at 160° (Found: Br, 62·6. $C_{21}H_{15}N_2Br_7S$ requires Br, 62·9%). This displayed the usual behaviour of the bromo-addition compounds on exposure to air, on treatment with sulphurous acid, and on boiling with alcohol and subsequent treatment with sodium hydroxide.

Dibromo-2-α-*naphthylamino*-β-*naphthathiazole.* — Either of the above bromides (1 g.) was digested with 20 c.c. of boiling alcohol for a short time, the crystalline hydrobromide so obtained was treated with warm 2*N*-sodium hydroxide for a few minutes, the product washed, dried, and crystallised from benzene–ethyl acetate (1 : 1); from this the *dibromo*-substitution product separated in small prisms which sintered at 180°, became yellow at 240°, and melted at 270—272° (Found: Br, 35·9. $C_{21}H_{12}N_2Br_2S$ requires Br, 35·6%).

Red Tribromide of 2-α-Naphthylamino-β-naphthathiazole.—A suspension of 1 g. of the dinaphthylthiocarbamide in 6 c.c. of warm chloroform was treated with 1 c.c. of bromine diluted with a little chloroform; the yellow, crystalline precipitate that formed at the half stage turned red when the addition of the bromine was completed. The mixture was boiled for a minute, cooled, and the vermilion, microcrystalline precipitate dried in a vacuum over potassium hydroxide. The *tribromide* became orange at 180°, yellow at 190°, pale ochre-yellow at 215°, and showed signs of softening at 260°, but was still unmelted above 280° (Found: Br, 41·8. $C_{21}H_{14}N_2Br_2S$,HBr requires Br, 42·4%). This tribromide lost bromine on exposure to air and was reduced by sulphurous acid in the usual way.

2-α-*Naphthylamino*-β-*naphthathiazole.*—Any one of the bromo-addition products obtained from the dinaphthylthiocarbamide by bromination in chloroform was suspended in sulphurous acid, and sulphur dioxide passed through the mixture until all solid matter was colourless. The reduction product was collected, digested with 2*N*-sodium hydroxide on a steam-bath for a few minutes, and the product washed, dried, and crystallised from ethyl acetate–toluene (1 : 1). The *naphthathiazole*, which separated in hard prisms, m. p. 217°, was recrystallised from benzene–ethyl acetate and obtained in colourless prisms, m. p. 221° (Found: S, 9·6. $C_{21}H_{14}N_2S$ requires S, 9·8%).

Bromination. From a solution of the naphthathiazole (0·3 g.) and bromine (0·5 c.c.) in chloroform, bright red prisms of the *hexabromide* separated slowly; they were dried in the usual way (Found: Br, 60·3. $C_{21}H_{14}N_2Br_6S$ requires Br, 59·6%). The hexabromide showed colour change without melting at 238° and behaved as usual on exposure to air and on treatment with sulphurous acid and with alcohol and sodium hydroxide.

s-Di-β-naphthylthiocarbamide was prepared from β-naphthylamine in the usual way. In the first experiments the thiocarbamide was recrystallised from glacial acetic acid, from which it separated in small prisms, m. p. 194°; in later experiments the product was treated as in the previous case and obtained as a micro-crystalline, white powder, m. p. 198°.

2-β-*Naphthylamino*-α-*naphthathiazole Hexabromide.*—(A) *s*-Di-β-naphthylthiocarbamide (m. p. 194°) (1 g.) containing a trace of acetic acid was suspended in 6 c.c. of chloroform and treated with 1 c.c. of bromine diluted with a small quantity of the same solvent as in the previous cases; the clear dark brown solution obtained became hot and evolved hydrogen bromide. The solution was refluxed for 2 minutes and cooled in a freezing mixture; the *hexa-*

bromide which then separated in fine, dark red crystals was dried in a vacuum over potassium hydroxide. It became light yellow at 190°, soft at 210°, and decomposed without melting at 216° (Found: Br, 60·3. $C_{21}H_{14}N_2Br_6S$ requires Br, 59·6%).

(B) The above bromination was repeated and the solution shaken to induce sudden crystallisation. The product consisted of small, purplish-red plates, which were dried in a vacuum as before. This hexabromide showed lightening in colour at 140°, further colour change at 194°, and melted to a clear red liquid at 196° (Found: Br, 59·8%).

Both forms of the hexabromide were reduced by sulphurous acid in the usual way, and exhibited the remarkable stability in air already referred to.

2-β-*Naphthylamino-α-naphthathiazole.*—The hexabromide was suspended in sulphurous acid and treated with a current of sulphur dioxide as in the previous case. The product was warmed with 2*N*-sodium hydroxide, washed, dried, and crystallised from toluene–ethyl acetate (1 : 1), from which it separated in large, silky plates, m. p. 221°. After recrystallisation from ethyl acetate–benzene, it was obtained in plates, m. p. 223° (Found: S, 8·9. $C_{21}H_{14}N_2S$ requires S, 9·8%).

Red Tribromide of 2-β-*Naphthylamino-α-naphthathiazole.*—One g. of *s*-di-β-naphthylthiocarbamide (microcrystalline powder, m. p. 198°) was suspended in 6 c.c. of chloroform and brominated in the usual way. The solution deposited the *tribromide* as a vermilion, microcrystalline powder which, after drying in a vacuum over potassium hydroxide, showed a colour change at about 170° and melted at 245° (Found: Br, 42·8. $C_{21}H_{14}N_2Br_2S,HBr$ requires Br, 42·4%).

Bromination of 2-β-*Naphthylamino-α-naphthathiazole.* — The naphthathiazole (0·5 g.) was treated with excess of bromine (1 c.c.) as in the previous case: on scratching, the hexabromide separated in small, dark purple-red prisms, m. p. 198°, after drying (Found: Br, 60·2. Calc., Br, 59·6%).

In conclusion, the author desires to express his gratitude to Prof. J. F. Thorpe, F.R.S., for the kind interest he has taken in the progress of these experiments.

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LONDON, S.W. 7. [*Received, June 3rd,* 1925.]

CCCXIII.—*An Investigation of the Action of Halogens on 2 : 4-Dimethylbenzoyl Chloride.*

By William Henry Perkin, jun., and John Frederic Smerdon Stone.

In a communication published a short time since (J., 1922, **121**, 2203), Davies and Perkin showed that ω-derivatives of the toluic acids such as

$$C_6H_4<\begin{matrix}CH_2X\\CO_2H\end{matrix} \qquad C_6H_4<\begin{matrix}CHX_2\\CO_2H\end{matrix} \qquad C_6H_4<\begin{matrix}CX_3\\CO_2H\end{matrix}$$

may be conveniently prepared from the corresponding toluoyl chlorides, $CH_3{\cdot}C_6H_4{\cdot}COCl$, or bromides by treatment with chlorine or bromine at temperatures varying from 160—220°, according to the degree of substitution desired, and subsequent decomposition of the substituted acid chlorides or bromides by formic acid, methyl alcohol, amines, etc. This simple process has made it possible to prepare conveniently many mono- and di-substitution derivatives of benzoic acid, such, for example, as the aldehydo-acids $CHO{\cdot}C_6H_4{\cdot}CO_2H$, which had previously been difficult of access.

In developing this process, it became interesting to determine the course substitution would take in the case of the dimethylbenzoic acids, $(CH_3)_2C_6H_3{\cdot}CO_2H$, that is to say, to find out whether substitution would occur in both methyl groups or be confined to one, and whether it would be possible, by the selection of suitable conditions of temperature, exposure to light, etc., to prevent simultaneous substitution in the ring. In order to examine this problem, we selected in the first instance 2 : 4-dimethylbenzoic acid (*m*-xylene-*o*-carboxylic acid) for investigation, and, as no method was available for the preparation of the large quantities of this acid required for this research, we have worked out the conditions most favourable for its formation. As the result of a large number of comparative experiments, we find that this acid may be obtained from *m*-xylene in a yield of 65% of that theoretically possible under the following conditions. *m*-Xylene is first converted, by acetyl chloride in the presence of anhydrous ferric chloride (compare Meissel, *Ber.*, 1899, **32**, 2420), into 2 : 4-dimethylacetophenone, $C_6H_3Me_2{\cdot}CO{\cdot}CH_3$, which, when treated with the calculated quantity of carefully prepared sodium hypobromite, is smoothly converted into practically pure 2 : 4-dimethylbenzoic acid. If, however, the hypobromite is present in excess or contains bromate, the acid is contaminated with a bromo-acid, m. p. 180°, which is evidently the 6-bromo-2 : 4-dimethylbenzoic acid,

m. p. 183—184°, obtained by Noyes (*Amer. Chem. J.*, 1898, 20, 802) by the oxidation of 6-bromo-2 : 4-dimethylacetophenone.

The method used for the direct substitution in the ω-positions in 2 : 4-dimethylbenzoic acid is essentially that worked out by Davies and Perkin (*loc. cit.*) in the case of the toluic acids. The acid is first converted into the acid chloride, $C_6H_3Me_2\cdot COCl$, by the action of thionyl chloride, and this is then treated with chlorine or bromine at temperatures varying from 160—220° according to the degree of substitution desired. The formation of the lower halogen substitution products takes place readily in bright sunlight but, if several atoms of chlorine or bromine are to be introduced, the use of a quartz mercury lamp is essential. In some cases, the bromo-derivatives were more readily prepared and separated than the corresponding chloro-derivatives.

Thus, for example, while we were unsuccessful in separating the ω-chloro- and ωω-dichloro-dimethylbenzoyl chlorides by fractional distillation, we found that the corresponding dibromo-derivatives, owing to greater difference in boiling point, could be comparatively easily separated. Careful treatment of the substituted acid chlorides with formic acid, alcohols or amines readily leads to the corresponding acids, esters, or amides. In this way we have prepared a large number of ω-halogen derivatives of 2 : 4-dimethylbenzoic acid, and the hydrolysis of these has yielded an interesting series of substances in which the methyl groups have been successively oxidised with production of alcohols, aldehydes, and acids.

I. *The ω-Bromo-2 : 4-dimethylbenzoic Acids.*

When 2 : 4-dimethylbenzoyl chloride is brominated at 160° with the aid of a mercury lamp, the bromo-acid bromide, distilling at 169—171°/15 mm., consists mainly of *2-bromomethyl-4-methylbenzoyl bromide*, $CH_3\cdot C_6H_3(CH_2Br)\cdot COBr$, but the fraction 160—180°/15 mm. contains this substance and *4-bromomethyl-2-methylbenzoyl bromide*, $CH_2Br\cdot C_6H_3(CH_3)\cdot COBr$, in the proportion of about 85 to 15%.*

On decomposing with formic acid, this mixture yields *2-bromomethyl-4-methylbenzoic acid*, m. p. 143—145°, the constitution of which is demonstrated by the fact that it yields *4-methyl-1 : 2-phthalide*, m. p. 118°, $CH_3\cdot C_6H_3<\begin{matrix}CH_2\\CO\end{matrix}>O$, at the melting point.

* In order to economise space, the formulæ in this communication are not written out hexagonally but the methyl-carbon atom to the left in the formula $CH_3\cdot C_6H_3(CH_3)\cdot CO_2H$ is numbered 4, whereas that to the right is numbered 2.

When an acid chloride is treated with bromine, it is converted into the acid bromide as pointed out by Davies and Perkin (*loc. cit.*, p. 2203).

The crystalline methyl ester (m. p. 62—63°) obtained directly by decomposing the mixed acid bromides with methyl alcohol is *methyl 2-bromomethyl-4-methylbenzoate*, because it decomposes on boiling into methyl bromide and 4-methyl-1 : 2-phthalide. This phthalide, on hydrolysis with alkali yields *2-hydroxymethyl-4-methylbenzoic acid*, which melts at 132—133° with regeneration of the phthalide.

The *methyl* ester of *4-bromomethyl-2-methylbenzoic acid* (m. p. 56°) is obtained by decomposing the mixed bromomethyl-methylbenzoyl bromides (see above) with methyl alcohol and boiling the mixed methyl esters, when methyl 2-bromomethyl-4-methylbenzoate passes completely into the phthalide whereas methyl 4-bromomethyl-2-methylbenzoate remains unchanged. On boiling with potassium hydroxide, the latter yields *4-hydroxymethyl-2-methylbenzoic acid*, $OH{\cdot}CH_2{\cdot}C_6H_3(CH_3){\cdot}CO_2H$, m. p. 142°, which does not lose water at its melting point. During this hydrolysis, a dibasic acid, $C_{18}H_{18}O_5$, m. p. 222°, is also obtained in small quantity and this is evidently *4 : 4′-dicarboxy-3 : 3′-dimethyldibenzyl ether*, $CO_2H{\cdot}(CH_3)C_6H_3{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}C_6H_3(CH_3){\cdot}CO_2H$, produced by the elimination of water from two molecules of the 4-hydroxymethyl acid. A somewhat similar observation was made by Günther (*Ber.*, 1890, **23**, 1061), who found that, when *p*-cyanobenzyl chloride, $CN{\cdot}C_6H_4{\cdot}CH_2Cl$, is hydrolysed with alkali, it yields 4 : 4′-dicarboxydibenzyl ether, $CO_2H{\cdot}C_6H_4{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2H$.

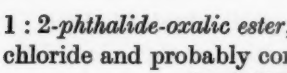
II. 2 : 4-*Di*(*bromomethyl*)*benzoic Acid*, $CH_2Br{\cdot}C_6H_3(CH_2Br){\cdot}CO_2H$.

The substitution of two atoms of bromine for hydrogen in 2 : 4-dimethylbenzoic acid leads mainly (compare p. 2286) to the formation of the *sym*-ω-dibromo-acid. The acid bromide of this acid, b. p. 223—228°/15 mm., is obtained when 2 : 4-dimethylbenzoyl chloride is heated with the calculated amount of bromine at a temperature rising from 150—190°, with the aid of the mercury lamp. On treatment with formic acid, this yields *2 : 4-di*(*bromomethyl*)*benzoic acid*, m. p. 158°, the methyl ester of which, on distillation, loses methyl bromide with the formation of *4-bromomethyl-1 : 2-phthalide*, $CH_2Br{\cdot}C_6H_3{<}\begin{matrix}CH_2\\CO\end{matrix}{>}O$, m. p. 159°, and this, on boiling with chalk and water, passes into *4-hydroxymethyl-1 : 2-phthalide*,

$$OH{\cdot}CH_2{\cdot}C_6H_3{<}\begin{matrix}CH_2\\CO\end{matrix}{>}O,$$

m. p. 125°. This substance is readily hydrolysed by warm sodium hydroxide to *2 : 4-di*(*hydroxymethyl*)*benzoic acid*, m. p. 146°. 4-Hydroxymethyl-1 : 2-phthalide condenses readily with oxalic ester in the presence of potassium ethoxide, yielding *4-hydroxymethyl-*

1 : 2-*phthalide-oxalic ester*, which gives a violet coloration with ferric chloride and probably consists essentially of the enolic modification,



In order to determine whether both bromine atoms in 2 : 4-di-(bromomethyl)benzoic acid are replaceable by cyanogen groups, the acid was digested with excess of potassium cyanide, but examination of the product showed that only the 4-ω-bromo-atom had been replaced by cyanogen, the product being 4-*cyanomethyl*-1 : 2-*phthalide*, m. p. 124°, $CN\cdot CH_2\cdot C_6H_3<^{CH_2}_{CO}>O$. This on shaking with hydrogen peroxide and sodium hydroxide yields the *amide*, from which 1 : 2-*phthalide*-4-*acetic acid*, m. p. 162°,

$$CO_2H\cdot CH_2\cdot C_6H_3<^{CH_2}_{CO}>O,$$

is obtained by the action of sodium nitrite.

III. *The Chlorination of* 2 : 4-*Dimethylbenzoyl Chloride.*

The attempt to prepare in a pure condition higher brominated derivatives of 2 : 4-dimethylbenzoic acid than those described in the last Section failed, mainly for the reason that the higher brominated acid bromides suffered vigorous decomposition when the attempt was made to distil them even under low pressures. Attention was therefore directed to the corresponding chloro-derivatives and we have fortunately been able to isolate these even up to the stage of the hexachloro-acid chloride, $CCl_3\cdot C_6H_3(CCl_3)\cdot COCl$. This has enabled us to study the whole series of these interesting substances and to investigate thoroughly their decomposition products and especially the products of their hydrolysis.

When 2 : 4-dimethylbenzoyl chloride is treated with the calculated amount of chlorine for the introduction of three atoms at a temperature rising from 180—210° and in ultra-violet light, and the product distilled, a fraction is obtained, b. p. 184—186°/16 mm., the chlorine content of which corresponds with that of the expected ω-trichloro-2 : 4-dimethylbenzoyl chloride. The first suspicion that this fraction is in reality an almost constant-boiling mixture of the di- and tetra-chlorinated dimethylbenzoyl chlorides, $CH_2Cl\cdot C_6H_3(CH_2Cl)\cdot COCl$ and

$$CHCl_2\cdot C_6H_3(CHCl_2)\cdot COCl,$$

containing only small quantities of the trichlorinated derivative, arose on attempting to prepare the substituted chlorophthalides by boiling the corresponding methyl esters. When the methyl esters, prepared in the usual manner from the acid chloride

fraction and methyl alcohol, are distilled, the crystals which separate from the distillate consist of 4-*chloromethyl*-1 : 2-*phthalide*, $CH_2Cl{\cdot}C_6H_3{<}\begin{matrix}CH_2\\CO\end{matrix}{>}O$, m. p. 144°, derived from the methyl ester, $CH_2Cl{\cdot}C_6H_3(CH_2Cl){\cdot}CO_2Me$, and corresponding with the 4-bromomethyl-1 : 2-phthalide described on p. 2277, the yield being about 30%. On the other hand, when the chloride fraction, b. p. 184—186°/16 mm., was digested with chalk and water, it gave a large yield of 2 : 4-dialdehydobenzoic acid, $CHO{\cdot}C_6H_3(CHO){\cdot}CO_2H$, an interesting substance which had not previously been obtained and the properties of which are described on p. 2290. The formation of this dialdehydo-acid is clear evidence that the acid chloride must have contained considerable quantities of 2 : 4-di(dichloromethyl)benzoyl chloride, $CHCl_2{\cdot}C_6H_3(CHCl_2){\cdot}COCl$. That the acid chloride fraction also contains 4-dichloromethyl-2-chloromethylbenzoyl chloride, $CHCl_2{\cdot}C_6H_3(CH_2Cl){\cdot}COCl$, was demonstrated in the following manner. The product of the action of chalk and water on this chloride fraction contains, besides 2 : 4-dialdehydobenzoic acid, a small quantity of a substance, $C_9H_6O_3$, melting at 159—160°, which, on investigation, proved to be 4-*aldehydo*-1 : 2-*phthalide*, $CHO{\cdot}C_6H_3{<}\begin{matrix}CH_2\\CO\end{matrix}{>}O$, and this must have been derived from the trichloro-acid chloride just mentioned. On the other hand, there is no evidence of the existence of the isomeric trichloro-acid chloride, $CH_2Cl{\cdot}C_6H_3(CHCl_2){\cdot}COCl$, in the above chloride fraction, because careful examination of the products of hydrolysis with chalk and water failed to reveal the presence of any substance derived from this chloride.

4-Aldehydo-1 : 2-phthalide combines readily with phenylhydrazine, yielding the yellow *hydrazone*, $PhN_2H{:}CH{\cdot}C_6H_3{<}\begin{matrix}CH_2\\CO\end{matrix}{>}O$, but its most interesting property is the fact that, when heated on the steam-bath even with 2*N*-sodium hydroxide, it undergoes the Cannizzaro reaction and yields a mixture of 2 : 4-di(hydroxymethyl)benzoic acid, $OH{\cdot}CH_2{\cdot}C_6H_3(CH_2{\cdot}OH){\cdot}CO_2H$ (m. p. 146°; compare p. 2290), and 2-*hydroxymethylterephthalic acid*,

$$CO_2H{\cdot}C_6H_3(CH_2{\cdot}OH){\cdot}CO_2H.$$

On heating in the steam-oven, the latter acid is converted into 4-*carboxy*-1 : 2-*phthalide*, $CO_2H{\cdot}C_6H_3{<}\begin{matrix}CH_2\\CO\end{matrix}{>}O$, m. p. 280°, a substance which is readily reconverted into 2-hydroxymethylterephthalic acid on hydrolysis.

IV. 2 : 4-*Di(dichloromethyl)benzoic Acid.*

When 2 : 4-dimethylbenzoyl chloride is chlorinated at 160—220° in ultra-violet light, until the increase of weight corresponds with the introduction of 4 atoms of chlorine, and the product fractionated, 2 : 4-*di(dichloromethyl)benzoyl chloride*, $CHCl_2 \cdot C_6H_3(CHCl_2) \cdot COCl$, b. p. 192—193°/10 mm., is obtained in good yield. Unlike the lower chlorinated dimethylbenzoyl chlorides, this substance is remarkably resistant to moisture and may be left exposed to air for some days without appreciable decomposition but it is decomposed by anhydrous formic acid under carefully regulated conditions to yield 2 : 4-*di(dichloromethyl)benzoic acid*, m. p. 160°. The *methyl* ester of this acid, $CHCl_2 \cdot C_6H_3(CHCl_2) \cdot CO_2Me$, distils at 186—188°/12 mm. without decomposition, but, at higher temperatures, it loses methyl chloride with the formation of 4-*dichloromethyl*-1 : 2-*chlorophthalide*, $CHCl_2 \cdot C_6H_3 < \begin{matrix} CHCl \\ CO \end{matrix} > O$, an oil distilling at 297°/763 mm. When 2 : 4-di(dichloromethyl)benzoyl chloride is boiled with chalk and water, it is converted into 2 : 4-*dialdehydobenzoic acid*, $CHO \cdot C_6H_3(CHO) \cdot CO_2H$, m. p. 141° (compare p. 2292). The yield of this important new acid, which appears to be the first of the dialdehydobenzoic acids to be prepared, calculated on the weight of the chloride employed in its preparation, is at least 70% of the theoretical. On treatment with aniline, it yields a *dianilino*-derivative which, since it is insoluble in sodium carbonate, probably has the constitution $NPh{:}CH \cdot C_6H_3 < \begin{matrix} CH \cdot NHPh \\ CO \end{matrix} > O$, the acid having acted in its hydroxy-phthalide modification much in the same way as *m*-opianic acid does in the same circumstances (Fargher and Perkin, J., 1921, **119**, 1729). The *disemicarbazone* is colloidal and could not be crystallised. It decomposes at 335° and is soluble in sodium carbonate, consequently it appears to be directly derived from the dialdehydo-acid and to have the normal constitution.

2 : 4-Dialdehydobenzoic acid reacts readily with phenylhydrazine to yield a yellow, crystalline derivative, m. p. 266°, insoluble in sodium carbonate, which is evidently *anhydro*-2 : 4-*dialdehydobenzoic acid diphenylhydrazone*, $PhN_2H{:}CH \cdot C_6H_3 < \begin{matrix} CH{:}N \\ CO \cdot NPh \end{matrix}$. It is proposed to investigate carefully the action of alkalis on 2 : 4-dialdehydobenzoic acid, in order to determine whether one or both of the aldehydo-groups are susceptible to the Cannizzaro reaction.

V. *The Pentachloro-2 : 4-dimethylbenzoyl Chlorides.*

An acid chloride fraction, b. p. 188—192°/14 mm., is obtained when chlorine is passed into 2 : 4-dimethylbenzoyl chloride, in the presence of ultra-violet light, at 220° until the increase in weight corresponds with the absorption of five atoms of chlorine. Investigation of this product has proved that it contains about equal quantities of the isomeric chlorides, $CCl_3 \cdot C_6H_3(CHCl_2) \cdot COCl$ and $CHCl_2 \cdot C_6H_3(CCl_3) \cdot COCl$. On hydrolysis with chalk and water, this mixture yields a sparingly soluble, crystalline acid, m. p. 242°, which examination has proved to be *2-aldehydoterephthalic acid*, $CO_2H \cdot C_6H_3(CHO) \cdot CO_2H$. This new acid reacts readily with phenylhydrazine with the formation of a colourless substance, $C_{15}H_{10}O_3N_2$, m. p. 327°, which is evidently *anhydro-2-aldehydoterephthalic acid phenylhydrazone*, $CO_2H \cdot C_6H_3 < \begin{matrix} CH{:}N \\ | \\ CO \cdot NPh \end{matrix}$. On treatment with hydroxylamine, 2-aldehydoterephthalic acid yields the normal *oxime*, $CO_2H \cdot C_6H_3(CH{:}N \cdot OH) \cdot CO_2H$, and, on heating, this melts and decomposes at about 136° with evolution of heat, solidifies again, and then melts at about 242°, isomeric change into the *imide* of *trimellitic acid*, a substance which does not appear to have been described, taking place. This characteristic change is analogous to the conversion by heat of the oximes of opianic acid and ψ-opianic acid into hemipinimide (Liebermann, *Ber.*, **1886**, **19**, 2926; Perkin, J., 1890, **57**, 1071) and of the oxime of *m*-opianic acid into *m*-hemipinimide (Perkin, J., 1916, **109**, 930). 2-Aldehydoterephthalic acid does not undergo the Cannizzaro reaction so readily as 4-aldehydo-1 : 2-phthalide (p. 2279), but when boiled with sodium hydroxide (25%) it is converted into a mixture of *2-hydroxymethylterephthalic acid*, $CO_2H \cdot C_6H_3(CH_2 \cdot OH) \cdot CO_2H$, and trimellitic acid, $CO_2H \cdot C_6H_3(CO_2H) \cdot CO_2H$.

The mother-liquors from which the 2-aldehydoterephthalic acid had separated contain, besides this acid, varying quantities of trimellitic acid produced evidently by the air oxidation of the aldehydo-acid and probably also of the isomeric *4-aldehydophthalic acid*, $CHO \cdot C_6H_3(CO_2H) \cdot CO_2H$. This latter acid is contained in these mother-liquors in considerable quantity, although, owing to its ready solubility and small facility for crystallising, it has not yet been found possible to isolate it in a pure condition.

The presence of this interesting isomeride of 2-aldehydoterephthalic acid was demonstrated in the first place by treating the impure acid with phenylhydrazine, when a substance crystallising in yellow needles, m. p. 118°, was isolated in quantity; this is readily soluble in sodium carbonate and consists of the *hydrate* of the

phenylhydrazone of 4-*aldehydophthalic acid*, $C_{15}H_{12}O_4N_2,H_2O$. This characteristic substance becomes anhydrous in a vacuum desiccator over sulphuric acid, melts at 174° with elimination of water and formation of the *anhydride*, $PhN_2H{:}CH{\cdot}C_6H_3(CO)_2O$, m. p. 217°, and this anhydride formation takes place quantitatively on heating in the air-oven at 115°.

VI. 2 : 4-*Di*(*trichloromethyl*)*benzoic Acid*.

The chloride of this acid, $CCl_3{\cdot}C_6H_3(CCl_3){\cdot}COCl$, b. p. 192—196°/15 mm., is obtained as a colourless oil which does not fume in moist air and in a yield of 70—80% when 2 : 4-dimethylbenzoyl chloride is chlorinated in ultra-violet light at 220° until six chlorine atoms have been absorbed. The stability of this chloride is also demonstrated by its behaviour with alkalis, since it may be boiled for a short time with dilute sodium carbonate without dissolving, although some chlorine is eliminated from the side chain during the process.

However, on leaving with anhydrous formic acid for about 2 weeks at the ordinary temperature, hydrolysis gradually takes place and 2 : 4-*di*(*trichloromethyl*)*benzoic acid* is obtained in colourless needles, m. p. 171°. The *methyl* ester, $CCl_3{\cdot}C_6H_3(CCl_3){\cdot}CO_2Me$, obtained by mixing the hexachloro-acid chloride with methyl alcohol, does not crystallise and decomposes, on heating, with elimination of methyl chloride and formation of 4-*trichloromethylphthalyl chloride* of the probable formula $CCl_3{\cdot}C_6H_3{<}\begin{matrix}CCl_2\\CO\end{matrix}{>}O$. This interesting substance, b. p. 186—187°/12 mm., does not appear to be hydrolysed by anhydrous formic acid, but it reacts readily with aniline to yield a *dianilide* which crystallises in colourless needles, m. p. 220°, and appears to be 4-*trichloromethylphthaldianilide* and to have the constitution $CCl_3{\cdot}C_6H_3(CO{\cdot}NHPh)_2$. Although the hexachloride (see above) is so resistant to hydrolysis, it reacts readily with ammonia or with aniline and is gradually hydrolysed by chalk and water. Thus the *amide*, $CCl_3{\cdot}C_6H_3(CCl_3){\cdot}CO{\cdot}NH_2$, is obtained in colourless needles when dry ammonia is passed into the solution of the acid chloride in benzene. This amide melts at 176° with elimination of hydrogen chloride, due probably to the formation of the substance $CCl_3{\cdot}C_6H_3{<}\begin{matrix}CCl_2\\C{:}NH\end{matrix}{>}O,HCl$ (compare Gabriel and Landsberger, *Ber.*, 1898, **31**, 2732). The addition of aniline to the solution of the hexachloro-acid chloride in benzene yields the *anilide* of 2 : 4-*di*(*trichloromethyl*)*benzoic acid*,

$$CCl_3{\cdot}C_6H_3(CCl_3){\cdot}CO{\cdot}NHPh,$$

m. p. 203°. When the hexachloro-acid chloride is boiled with

chalk and water, gradual hydrolysis takes place, each $-CCl_3$ group becoming $-CO_2H$, and ultimately an almost quantitative yield of trimellitic acid, $CO_2H \cdot C_6H_3(CO_2H) \cdot CO_2H$, is obtained.

EXPERIMENTAL.

2 : 4-*Dimethylacetophenone*, $CH_3 \cdot C_6H_3(CH_3) \cdot CO \cdot CH_3$.—Anhydrous ferric chloride (100 g.) is just covered with dry carbon disulphide in a 2-litre flask, fitted with a reflux condenser and dropping funnel, and a mixture of *m*-xylene (100 g.) and a slight excess of acetyl chloride (84 g.) is slowly run in with occasional vigorous shaking, the operation taking about ¾ hour. The whole is heated on the steam-bath until the evolution of hydrogen chloride ceases (approx. 2 hours), the thick dark liquid poured into water, and after addition of ether, the black ether layer is well washed with water and dilute sodium hydroxide, dried over calcium chloride, and the ether removed. Meissel (*Ber.*, 1899, **32**, 2420) recommends distilling the dark oil in steam, but this is unnecessary, since ordinary distillation suffices, the portion distilling at 220—230° being sufficiently pure for most purposes and on redistillation the pure ketone distils at 228°/760 mm. (Found : C, 81·0; H, 8·2. $C_{10}H_{12}O$ requires C, 81·0; H, 8·1%).

2 : 4-*Dimethylbenzoic Acid*, $CH_3 \cdot C_6H_3(CH_3) \cdot CO_2H$.—After several comparative experiments, the best oxidising agent for converting 2 : 4-dimethylacetophenone into this acid was found to be sodium hypobromite, but unless the temperature is kept as near 0° as possible both in the preparation of the hypobromite and in the subsequent oxidation, a brominated 2 : 4-dimethylbenzoic acid is also obtained which melts at 180° and is apparently identical with the 6-bromo-2 : 4-dimethylbenzoic acid, m. p. 183—184°, described by Noyes (*Amer. Chem. J.*, 1898, **20**, 802) (Found : C, 47·1; H, 4·1. $C_9H_9O_2Br$ requires C, 47·2; H, 3·9%). Sodium hydroxide (80 g.) is dissolved in water (1600 c.c.) cooled to 0°, and then bromine (160 g.) carefully run in in small quantities with vigorous shaking, 2 : 4-dimethylacetophenone (50 g.) is now added and the whole shaken continuously for 2 hours. The operation is seen to be at an end when the surface layer of the ketone gives place to a heavy layer of bromoform. After this has been run off, the aqueous solution is saturated with sulphur dioxide, when 2 : 4-dimethylbenzoic acid is precipitated as a voluminous, crystalline precipitate; after washing and drying, it is pure enough for most purposes. For the chlorination experiments it was, however, found better to recrystallise it from dilute alcohol, from which it separates in long needles, m. p. 126° (Found : C, 71·9; H, 6·8. $C_9H_{10}O_2$ requires C, 72·0; H, 6·7%).

The *methyl* ester, $CH_3 \cdot C_6H_3(CH_3) \cdot CO_2Me$, is readily prepared by adding the acid chloride (see below) to methyl alcohol and precipitating with water. The ether extract is well washed with water and sodium carbonate, dried over calcium chloride, the ether removed, and the oil distilled, when the methyl ester passes over at 232—233°/762 mm. and melts at — 2° to — 1° (Found: C, 73·0; H, 7·3. $C_{10}H_{12}O_2$ requires C, 73·2; H, 7·3%).

2-Bromomethyl-4-methylbenzoyl Bromide, $CH_3 \cdot C_6H_3(CH_2Br) \cdot COBr$. —The 2 : 4-dimethylbenzoyl chloride required in large quantities for this and the subsequent operations was obtained in a yield of 90% by boiling the acid with 10% excess of thionyl chloride. The dark oil remaining after distilling off the excess distilled at 234—236°/760 mm. or at 113—115°/15 mm. and melted at about 25·5° (compare Ador and Meier, *Ber.*, 1879, **18**, 1970). The bromination of this chloride is carried out in a flask fitted with a reflux condenser and dropping funnel the end of which is well below the surface of the chloride (33·7 g.). At 160°, bromine (32 g.) is slowly run in and, provided the operation is done in plenty of sunlight, substitution rarely takes more than an hour and the temperature need not be raised above 180°. In ultra-violet light double this quantity of the chloride can be brominated in an hour at a temperature not exceeding 160°. The separation and purification of this acid bromide is rendered tedious owing to the presence of small quantities of its isomeride, *4-bromomethyl-2-methylbenzoyl bromide*, $CH_2Br \cdot C_6H_3(CH_3) \cdot COBr$, which has not been obtained in a pure condition, although certain derivatives are described later in this paper. After three or four fractionations under reduced pressure, a yield of 50% of 2-bromomethyl-4-methylbenzoyl bromide, containing traces of the isomeride, is obtained as a slightly green oil distilling at 169—171°/15 mm. It is rapidly decomposed by moist air and should be used directly it has been prepared (Found: Br, 54·9. $C_9H_8OBr_2$ requires Br, 54·8%). In order to prove that this substance consisted entirely of bromo-acid bromide and did not contain any acid chloride, the silver halide (0·4386 g.) from the Carius determination was heated in a stream of chlorine at 200° for 2 hours, when 0·3496 AgCl resulted, whereas theory requires 0·3508. This fully confirms the observation of Davies and Perkin (*loc. cit.*) that acid chlorides are completely converted into acid bromides on treatment with bromine.

2-Bromomethyl-4-methylbenzoic Acid, $CH_3 \cdot C_6H_3(CH_2Br) \cdot CO_2H$.— This acid is readily obtained from the acid bromide by stirring with six times its weight of anhydrous formic acid, care being taken that the temperature does not rise above 15°, in order to avoid any hydrolysis of the side chain bromine atom. The operation

is complete in a few minutes and the precipitate of the acid is collected and crystallised from petroleum (b. p. 80—100°), from which it separates in small, colourless needles, m. p. 143—145° (decomp.) (Found : Br, 34·1. $C_9H_9O_2Br$ requires Br, 34·9%). The *methyl* ester, $CH_3 \cdot C_6H_3(CH_2Br) \cdot CO_2Me$, is obtained by adding the acid bromide to well-cooled methyl alcohol and, after standing over-night, the mixture is poured into water, ether added, and the ethereal extract well washed with water and dilute sodium carbonate, dried over anhydrous sodium sulphate, and evaporated. The syrup gradually crystallises in colourless needles which are drained and crystallised from petroleum, in which the substance is very soluble and from which it separates in rectangular prisms, m. p. 62—63° (Found : Br, 33·0. $C_{10}H_{11}O_2Br$ requires Br, 32·9%). The vapour of this methyl ester is very irritating and causes prolonged sneezing. When boiled in a test tube for a few minutes, it readily loses methyl bromide with formation of *4-methyl-1 : 2-phthalide*, $CH_3 \cdot C_6H_3 < \begin{matrix} CH_2 \\ CO \end{matrix} > O$, in theoretical yield. The melt solidifies, on cooling, and the phthalide is best recrystallised from petroleum, from which it separates in long, colourless needles, m. p. 117—118° (Found : C, 72·9; H, 5·5. $C_9H_8O_2$ requires C, 72·9; H, 5·4%). This substance dissolves readily on boiling with dilute sodium hydroxide and, on the addition of hydrochloric acid to the cold solution, *2-hydroxymethyl-4-methylbenzoic acid* separates in small needles (Found : C, 64·9; H, 5·9. $C_9H_{10}O_3$ requires C, 65·1; H, 6·0%). This acid melts at 132—133° with loss of water and regeneration of the phthalide.

Methyl 4-Bromomethyl-2-methylbenzoate, $CH_2Br \cdot C_6H_3(CH_3) \cdot CO_2Me$. —Reference has already been made (p. 2276) to the presence in the acid bromide, prepared as explained above, of small quantities of 4-bromomethyl-2-methylbenzoyl bromide. Although it was found impossible to isolate this from the mixture, the methyl ester of the bromo-acid may be obtained pure in the following manner. The bromo-acid bromide fraction, b. p. 160—180°/15 mm., is converted into the mixture of methyl esters in the way just described, and the mixture boiled until all the methyl 2-bromomethyl-4-methylbenzoate has been converted, by loss of methyl bromide, into 4-methyl-1 : 2-phthalide. This separates almost completely on mixing with light petroleum, and the filtrate, on evaporation, deposits methyl 4-bromomethyl-2-methylbenzoate as a crystalline mass which crystallises from methyl alcohol in needles, m. p. 55—56°, and is readily distinguished from its isomeride in that, on boiling, it does not decompose with loss of methyl bromide (Found : Br, 31·2. $C_{10}H_{11}O_2Br$ requires Br, 32·9%).

4-*Hydroxymethyl*-2-*methylbenzoic Acid*, $OH{\cdot}CH_2{\cdot}C_6H_3(CH_3){\cdot}CO_2H$. —Complete hydrolysis of the above methyl ester (4·5 g.) is readily effected by boiling with potassium hydroxide (3 g. in 50 c.c. of water) for 2 hours. After filtering, the cold solution is acidified with concentrated hydrochloric acid, the voluminous crystalline precipitate collected and crystallised from boiling water, from which 4-*hydroxymethyl*-2-*methylbenzoic acid* separates in glistening, rectangular plates, m. p. 141—142° (Found: C, 65·3; H, 6·1. $C_9H_{10}O_3$ requires C, 65·1; H, 6·0%).

During the recrystallisation of this acid, a small quantity of a white substance remains undissolved and this separates from dilute alcohol as a microcrystalline powder, m. p. 221—222°. It is explained in the introduction (p. 2277) that this substance is 4 : 4′-*dicarboxy*-3 : 3′-*dimethyldibenzyl ether* (Found: C, 68·1; H, 5·7. $C_{18}H_{18}O_5$ requires C, 68·8; H, 5·7%). On titration, 0·0252 required 1·6 c.c. of *N*/10-NaOH for neutralisation, whereas this amount of a dibasic acid, $C_{18}H_{18}O_5$ should neutralise 1·6 c.c. The molecular weight, determined by the method of Rast (*Ber.*, 1922, **55**, 1051, 3727), when 0·0047, dissolved in 0·0859 of camphor, caused a depression in the m. p. of camphor of 6·9°, was found as 317, whereas $C_{18}H_{18}O_5$ requires *M*, 314.

2 : 4-*Di*(*bromomethyl*)*benzoyl Bromide*, $CH_2Br{\cdot}C_6H_3(CH_2Br){\cdot}COBr$. —The bromination of 2 : 4-dimethylbenzoyl bromide to this stage cannot be effected with good results in sunlight, but with the aid of a mercury lamp and careful regulation of the temperature a yield of 40—50% of the above bromide may be obtained. Starting with the temperature at 150°, bromine (106 g.) is slowly dropped into 2 : 4-dimethylbenzoyl chloride (56 g.), the operation being complete in 2 hours if the temperature at the end of the experiment is allowed to rise to 190°. Above this, considerable darkening of the liquid takes place and subsequent fractionation is rendered difficult owing to the formation of much tar. The dark green liquid is distilled in small quantities under reduced pressure as quickly as possible and the fraction 215—230°/15 mm. again distilled, when the fraction 223—228°/15 mm. consists of almost pure 2 : 4-di(bromomethyl)benzoyl bromide (Found: Br, 64·0. $C_9H_7OBr_3$ requires Br, 64·7%). This bromide is a viscid, green syrup which fumes in moist air and shows no signs of crystallising even on long standing.

2 : 4-*Di*(*bromomethyl*)*benzoic Acid*, $CH_2Br{\cdot}C_6H_3(CH_2Br){\cdot}CO_2H$.— This acid, prepared in the usual manner by stirring the acid bromide with anhydrous formic acid at as low a temperature as possible (p. 2284), crystallises from benzene in small, colourless prisms, m. p. 158° (Found: Br, 52·4. $C_9H_8O_2Br_2$ requires Br, 52·0%).

The *methyl* ester, obtained by adding the dibromo-acid bromide to well-cooled methyl alcohol, separates from the mixture and crystallises from methyl alcohol in long, colourless, feathery needles, m. p. 83—84° (Found : Br, 49·7. $C_{10}H_{10}O_2Br_2$ requires Br, 49·7%). The vapour of this methyl ester is very pungent and produces prolonged sneezing, and solutions cause burns when brought in contact with the skin. When this methyl ester is boiled in a test-tube for a few minutes, it loses methyl bromide, and the melt, on cooling, crystallises in fan-shaped masses of needles. This consists of nearly pure 4-*bromomethyl*-1 : 2-*phthalide*, $CH_2Br{\cdot}C_6H_3{<}\begin{matrix}CH_2\\CO\end{matrix}{>}O$, which separates from methyl alcohol in small, glistening plates, m. p. 159°, and is very pungent when warmed (Found : Br, 34·9. $C_9H_7O_2Br$ requires Br, 35·2%).

4-*Hydroxymethyl*-1 : 2-*phthalide*, $OH{\cdot}CH_2{\cdot}C_6H_3{<}\begin{matrix}CH_2\\CO\end{matrix}{>}O$. —This substance may be obtained by boiling 2 : 4-di(bromomethyl)benzoyl bromide with precipitated chalk and water, but the method is unsatisfactory owing to the difficulty in purifying the product. Subsequently it was found that a much better yield of pure substance can be obtained by boiling 4-bromomethyl-1 : 2-phthalide (5 g.) with chalk (2 g.) and water (50 c.c.). After cooling, the solution is acidified with hydrochloric acid and the whole quickly filtered, when the filtrate gradually deposits small, colourless prisms (2·5 g.). 4-*Hydroxymethyl*-1 : 2-*phthalide*, m. p. 124—125°, is readily soluble in hot water or toluene but sparingly so in cold water or ether (Found : C, 66·1; H, 4·9. $C_9H_8O_3$ requires C, 65·9; H, 4·9%).

2 : 4-*Di*(*hydroxymethyl*)*benzoic Acid*,

$$OH{\cdot}CH_2{\cdot}C_6H_3(CH_2{\cdot}OH){\cdot}CO_2H.$$

—This, the parent substance of the above hydroxymethylphthalide, is prepared by warming the latter with sodium hydroxide, cooling well, and acidifying with hydrochloric acid. After being quickly collected, washed with water, and left on porous porcelain exposed to air, the small, colourless, glistening plates melt at 145—146° (Found : C, 59·2; H, 5·6. $C_9H_{10}O_4$ requires C, 59·3; H, 5·5%).

Ethyl 4-*Hydroxymethyl*-1 : 2-*phthalideoxalate*,

$$OH{\cdot}CH_2{\cdot}C_6H_3\begin{matrix}C(OH){\cdot}CO_2Et\\{>}O\\CO\end{matrix}.$$

—In preparing this substance, absolute alcohol (0·4 c.c.) is carefully added to molecular potassium (0·4 g.) under dry ether (30 c.c.) and after the evolution of hydrogen has ceased and a slight excess of potassium is present, oxalic ester (1·5 g.) is added. Combination follows at once, the potassium ethoxide passes into solution and

the colour changes to yellow. Hydroxymethylphthalide (1·7 g.) suspended in dry ether is now added and the whole left over-night. The voluminous, yellow precipitate is collected, dissolved in a little water, and the orange solution of the potassium derivative acidified. The viscid oil which gradually crystallises separates from dilute alcohol in small, colourless prisms, m. p. 169—170° (Found: C, 59·3; H, 4·6. $C_{13}H_{12}O_6$ requires C, 59·1; H, 4·6%). The methyl-alcoholic solution gives, on the addition of ferric chloride, a deep violet coloration, and the substance is immediately soluble in sodium hydroxide to a yellow solution.

4-Cyanomethyl-1 : 2-phthalide, $CH_2(CN)\cdot C_6H_3<\begin{matrix}CH_2\\CO\end{matrix}>O$.—2 : 4-Di(bromomethyl)benzoic acid (25 g.) was gradually added to potassium cyanide (14 g.) dissolved in alcohol (50 c.c.) and water (100 c.c.) and, after the somewhat vigorous reaction had subsided, the whole was heated on the steam-bath for 10 minutes, cooled, and diluted with water (100 c.c.). The solution, acidified with hydrochloric acid, was extracted with ether, and the ethereal layer well washed with water and dried over calcium chloride, when a small quantity of a red gum separated. The ether was then removed from the filtered solution; the oil, which gradually solidified, separated from benzene in small plates, m. p. 123—124° (Found: C, 69·5; H, 4·1; N, 8·0. $C_{10}H_7O_2N$ requires C, 69·4; H, 4·0; N, 8·1%). *1 : 2-Phthalide-4-acetamide* is readily prepared by shaking the cyano-derivative (3 g.) with hydrogen peroxide (30 c.c. of 6%) and sodium hydroxide (1 c.c. of 10%) at 40°. When all has dissolved and the evolution of oxygen has ceased, the solution is acidified with concentrated hydrochloric acid and the small, white plates are collected. This amide separates from alcohol in feathery needles, m. p. 218—219° (slight decomp.) (Found: C, 62·7; H, 4·8. $C_{10}H_9O_3N$ requires C, 62·8; H, 4·7%).

1 : 2-Phthalide-4-acetic Acid, $CO_2H\cdot CH_2\cdot C_6H_3<\begin{matrix}CH_2\\CO\end{matrix}>O$.—The hydrolysis of 4-cyanomethyl-1 : 2-phthalide by methyl-alcoholic potassium hydroxide yields a product which is difficult to purify, but the acid is readily obtained in a practically theoretical yield under the following conditions. The amide (0·24 g.) is dissolved in concentrated sulphuric acid and the whole heated on the steam-bath for a few minutes, cooled to 0°, and sodium nitrite (0·2 g.) dissolved in water (1 c.c.) added. After heating on the steam-bath for about 3 minutes, the product is poured into water (5 c.c.), when, on cooling, needles are deposited which are completely soluble in dilute sodium carbonate and, after recrystallisation from water, melt at 161—162° and consist of 1 : 2-phthalide-4-acetic

acid (Found : C, 62·3; H, 4·3. $C_{10}H_8O_4$ requires C, 62·5; H 4·2%).

The only indication that an unsymmetrical dibromo-derivative is formed during the bromination of 2 : 4-dimethylbenzoyl chloride was obtained when a large quantity of the dibrominated bromide (b. p. 215—230°/15 mm.) was hydrolysed with chalk and water (compare p. 2287).

On adding phenylhydrazine to the mother-liquor from which the 4-hydroxymethyl-1 : 2-phthalide had separated, a small quantity of a condensation product was obtained which crystallised from benzene–petroleum in small, yellow prisms, m. p. 179—180° (Found : C, 70·7; H, 5·4. $C_{15}H_{14}O_2N_2$ requires C, 70·8; H, 5·5%). This substance is evidently the phenylhydrazone either of $CHO{\cdot}C_6H_3(CH_3){\cdot}CO_2H$ or of $CH_3{\cdot}C_6H_3(CHO){\cdot}CO_2H$, probably the former, but the amount available was too small for further investigation.

Preparation of the Mixture of 2 : 4-*Di(chloromethyl)- and* 2 : 4-*Di(dichloromethyl)benzoyl Chlorides*, $CH_2Cl{\cdot}C_6H_3(CH_2Cl){\cdot}COCl$ and $CHCl_2{\cdot}C_6H_3(CHCl_2){\cdot}COCl$.—The apparatus employed in the preparation of all the chlorinated 2 : 4-dimethylbenzoyl chlorides described in this communication consisted of a quartz flask, of 300 c.c. capacity, having a wide neck about 12 inches long in which was fitted a cork bored with three holes for carrying a thermometer, an adapter for attaching to a reflux condenser, and a tube, for introducing the chlorine, reaching nearly to the bottom of the flask. The whole apparatus (without the condenser) with its contents could be weighed from time to time in order to determine the amount of chlorine absorbed, and chlorination was always carried out in close proximity to a powerful ultra-violet light mercury lamp.

When 2 : 4-dimethylbenzoyl chloride (p. 2284; 60 g.) was chlorinated under these conditions at a temperature starting at 180° and gradually rising to 210° until 3 atoms of chlorine had been absorbed, and the product fractionated, about 60% passed over at 184—186°/16 mm. as an almost colourless, fuming oil which gave analytical results corresponding with those required for a *trichloro-dimethylbenzoyl chloride* (Found : Cl, 51·7. $C_9H_6OCl_4$ requires Cl, 52·2%). As stated in the introduction (p. 2278), this oil is in reality a constant-boiling mixture consisting essentially of di- and tetra-chloro-acid chlorides and containing only a small quantity of the trichlorinated chloride. From this mixture the following derivatives were prepared.

4-*Chloromethyl*-1 : 2-*phthalide*, $CH_2Cl{\cdot}C_6H_3{<}\begin{matrix}CH_2\\CO\end{matrix}{>}O$.—The mixed chlorides were converted into the mixed methyl esters by boiling with

methyl alcohol; these were isolated in the usual manner (p. 2285). When the resulting oil was heated to boiling in small quantities, the methyl ester, $CH_2Cl{\cdot}C_6H_3(CH_2Cl){\cdot}CO_2Me$, readily decomposed * with elimination of methyl chloride and formation of solid 4-chloromethyl-1 : 2-phthalide; this may be freed from the oily admixture by rubbing with methyl alcohol and subsequent recrystallisation from this solvent, from which it separates in glistening plates, m. p. 143—144° (Found: C, 58·5; H, 3·9; Cl, 20·2. $C_9H_7O_2Cl$ requires C, 59·2; H, 3·8; Cl, 19·5%).

2 : 4-*Dialdehydobenzoic Acid*, $CHO{\cdot}C_6H_3(CHO){\cdot}CO_2H$.—The chlorinated acid chloride (b. p. 184—186°/16 mm.; 47 g.) was boiled with chalk (50 g.) and water (300 c.c.) for 4 hours, precaution against access of air being taken by the use of a Bunsen valve attached to the top of the condenser. The product was cooled, acidified with concentrated hydrochloric acid, and, after remaining over-night, a gummy solid (A) was filtered off and the filtrate extracted three times with ether. The white solid obtained after drying and removing the ether separated from 50% acetic acid in nodules, m. p. 138—139°, and consisted of 2 : 4-dialdehydobenzoic acid. This was proved by mixing with a specimen of the dialdehydo-acid prepared as described on p. 2292, when there was no depression in m. p., and also by conversion into the characteristic dianilino-derivative, m. p. 208°. The gummy solid (A) mentioned above was again heated with chalk and water for 3 hours, and the filtered solution acidified. The crystalline precipitate so obtained was extracted with boiling water and filtered from gum when, on cooling, a crystalline mass of impure 4-*aldehydo*-1 : 2-*phthalide* was deposited and this separated from water, in which it was only sparingly soluble, in small plates, m. p. 159—160°, the yield being about 10% of theory (Found: C, 66·4; H, 3·6. $C_9H_6O_3$ requires C, 66·7; H, 3·7%). This substance is insoluble in sodium bicarbonate but dissolves on warming with sodium hydroxide. The *phenylhydrazone* is obtained by adding phenylhydrazine to the solution of the substance in dilute acetic acid and separates from alcohol in lemon-yellow needles, m. p. 171—172° (Found: N, 11·2. $C_{15}H_{12}O_2N_2$ requires N, 11·1%).

The Action of Alkali on 4-*Aldehydo*-1 : 2-*phthalide*.—When this phthalide (0·5 g.) was mixed with 2*N*-sodium hydroxide (5 c.c.) and warmed for about ½ minute on the steam-bath, complete solution took place. Addition of hydrochloric acid to the cooled solution precipitated a crystalline solid which, after drying in the vacuum desiccator, was found to be nearly pure 2-*hydroxy*-

* The decomposition of the methyl ester, $CHCl_2{\cdot}C_6H_3(CHCl_2){\cdot}CO_2Me$, into the syrupy 4-dichloromethyl-1 : 2-chlorophthalide is described on p. 2292.

methylterephthalic acid (see below) (Found: C, 55·8; H, 4·4. $C_9H_8O_5$ requires C, 55·1; H, 4·1%).

This acid was heated in the air-oven at 110° for an hour, extracted with cold sodium bicarbonate, filtered, and the filtrate acidified. The indefinite, crystalline powder so obtained melted at 279—280° and consisted of 4-*carboxy*-1 : 2-*phthalide*,

$$CO_2H\cdot C_6H_3\langle\begin{matrix}CH_2\\CO\end{matrix}\rangle O$$

(Found: C, 60·6; H, 3·3. $C_9H_6O_4$ requires C, 60·7; H, 3·3%).

The lactone ring in this substance readily suffers hydrolysis when the substance is warmed with dilute sodium hydroxide, with the formation of the 2-hydroxymethylterephthalic acid, which apparently has no definite melting point but, on heating, gradually passes, with loss of water, into the lactone. Titration: 0·0884 required 8·9 c.c. of *N*/10-NaOH for neutralisation, whereas this amount of a dibasic acid, $C_9H_8O_5$, should neutralise 9·0 c.c.

2 : 4-*Di*(*dichloromethyl*)*benzoyl Chloride*, $CHCl_2\cdot C_6H_3(CHCl_2)\cdot COCl$. —2 : 4-Dimethylbenzoyl chloride (p. 2284) was chlorinated in ultra-violet light at a temperature initially at 200° and rising to 220° in the apparatus described on p. 2289, until the amount of chlorine absorbed corresponded with the substitution of four atoms of hydrogen.

On twice fractionating, 60—70% of the product distilled at 192—193°/10 mm. as a nearly colourless oil which is not readily attacked by moist air (Found: Cl, 57·8. $C_9H_5OCl_5$ requires Cl, 57·9%). When the benzene solution of this chloride was mixed with aniline, the *anilide* of 2 : 4-di(dichloromethyl)benzoic acid was obtained which separated from alcohol in colourless needles, m. p. 159° (Found: Cl, 38·7; N, 3·9. $C_{15}H_{11}ONCl_4$ requires Cl, 39·1; N, 3·9%). The fact that this derivative appeared to be a single substance may be taken as evidence that the chloride consists essentially, if not entirely, of 2 : 4-di(dichloromethyl)benzoyl chloride.

2 : 4-*Di*(*dichloromethyl*)*benzoic Acid*, $CHCl_2\cdot C_6H_3(CHCl_2)\cdot CO_2H$.—Owing to its stability to hydrolytic agents, some difficulty was experienced in converting the above acid chloride into the corresponding acid. Boiling with anhydrous formic acid decomposes the chloride fairly readily but also attacks the ω-chlorine atoms. Comparative experiments showed, however, that, if the temperature is not allowed to rise above 60°, hydrolysis is confined to the acid chloride group. The acid crystallises from the formic acid and is recrystallised from benzene–petroleum, separating in colourless needles, m. p. 159—160° (Found: Cl, 48·5. $C_9H_6O_2Cl_4$ requires Cl, 49·3%). The *methyl* ester, prepared by mixing the acid

chloride with methyl alcohol, is a colourless oil distilling at 186—188°/12 mm. (Found: Cl, 47·0. $C_{10}H_8O_2Cl_4$ requires Cl, 47·0%). This methyl ester is remarkably stable and may be distilled in small quantities at ordinary pressures with little decomposition, but when it is kept boiling, it gradually loses methyl chloride with the formation of 4-*dichloromethyl*-1 : 2-*chlorophthalide*,

$$CHCl_2 \cdot C_6H_3 \begin{<}{CHCl \atop CO-} \end{>} O,$$

which distils at 297°/763 mm. and was not obtained crystalline (Found: Cl, 42·7. $C_9H_5O_2Cl_3$ requires Cl, 42·9%).

2 : 4-*Dialdehydobenzoic Acid*, $CHO \cdot C_6H_3(CHO) \cdot CO_2H$ (compare p. 2290).—The hydrolysis of 2 : 4-di(dichloromethyl)benzoyl chloride (30 g.) with precipitated chalk (40 g.) and water (300 c.c.) proceeds smoothly at the temperature of the boiling mixture if precautions are taken to exclude air during the process. After boiling for about 3 hours and until no oily drops of the chloride are left, the product is cooled, filtered, excess of hydrochloric acid added, and the whole left over-night. The crystalline solid is collected and the filtrate extracted several times with ether, as the aldehydo-acid is soluble in the acid solution. The solid so obtained is difficult to crystallise. It is very sparingly soluble in chloroform, benzene, or petroleum but readily so in acetone, alcohol or formic acid. It is also very soluble in water and does not crystallise on cooling. It may, however, be recrystallised from acetic acid (50%), separating in small nodules, m. p. 140—141°, the yield, calculated on the chloride employed, being about 70% (Found: C, 60·6; H, 3·5. $C_9H_6O_4$ requires C, 60·7; H, 3·3%). The *dianilino*-derivative is obtained when the alcoholic solution of the acid is warmed with aniline and separates from methyl alcohol in colourless needles, m. p. 208° (Found: C, 76·7; H, 5·0; N, 8·5. $C_{21}H_{16}O_2N_2$ requires C, 76·8; H, 4·9; N, 8·5%). This derivative is insoluble in sodium carbonate and dissolves in concentrated sulphuric acid to a yellow solution the colour of which is discharged on adding water.

Condensation with phenylhydrazine. When phenylhydrazine (2 mols.) is added to the solution of dialdehydobenzoic acid (1 mol.) in hot dilute glacial acetic acid, an orange oil is immediately precipitated which solidifies at once to a mass of yellow needles insoluble in sodium carbonate. After recrystallisation from alcohol, in which it is sparingly soluble, this *anhydro*-2 : 4-*dialdehydobenzoic acid diphenylhydrazone* is obtained in canary-yellow prisms, m. p. 264—266° (Found: C, 73·9; H, 4·6; N, 16·4. $C_{21}H_{16}ON_4$ requires C, 74·1; H, 4·7; N, 16·5%).

Condensation with p-*nitrophenylhydrazine.* When an alcoholic solution of dialdehydobenzoic acid was added to a hot dilute solu-

tion of *p*-nitrophenylhydrazine hydrochloride, a flocculent, orange precipitate separated which could not be recrystallised. It is insoluble in cold dilute sodium carbonate but dissolves with a dark claret colour on warming. It is immediately soluble in cold dilute sodium hydroxide. It seems probable that this substance is the p-*nitrophenylhydrazone* of 4-*aldehydo*-1 : 2-*hydroxyphthalide* and has the constitution $NO_2 \cdot C_6H_4 \cdot N_2H{:}CH \cdot C_6H_3 \begin{matrix} CH(OH) \\ CO \end{matrix} > O$ (Found : C, 57·5; H, 3·8; N, 13·5. $C_{15}H_{11}O_5N_3$ requires C, 57·5; H, 3·5; N, 13·4%). This substance exhibits a curious behaviour in the melting-point tube, the reason for which is not clear. Having shrunk somewhat at 205—210°, it melts at 221—223°, solidifying almost at once and melting at 236—237°; after it has again solidified, its m. p. is about 180°. If *p*-nitrophenylhydrazine and dialdehydobenzoic acid, both dissolved in glacial acetic acid, are mixed, an orange powder separates which is only slowly hydrolysed by sodium hydroxide, melts at 235°, and appears to be an acetyl derivative of the above substance (Found : C, 57·5; H, 3·7; N, 11·8. $C_{17}H_{13}O_6N_3$ requires C, 57·5; H, 3·7; N, 11·8%). Lastly, if the condensation is performed in hot nitrobenzene solution, a substance is obtained in small, orange prisms, m. p. 295° (decomp.), which is evidently the dinitro-derivative of the anhydro-diphenylhydrazone,

$$NO_2 \cdot C_6H_4 \cdot N_2H{:}CH \cdot C_6H_3 \begin{matrix} CH{:}N \\ | \\ CO \cdot N \cdot C_6H_4 \cdot NO_2 \end{matrix}$$

(Found : N, 19·2. $C_{21}H_{14}O_5N_6$ requires N, 19·5%).

Pentachloro-2 : 4-*dimethylbenzoyl Chlorides*, $CCl_3 \cdot C_6H_3(CHCl_2) \cdot COCl$ *and* $CHCl_2 \cdot C_6H_3(CCl_3) \cdot COCl$.—The introduction of five atoms of chlorine into 2 : 4-dimethylbenzoyl chloride (61 g.) is complete in about 3¼ hours under the influence of ultra-violet light, the temperature towards the end of the process being raised to 220° and the chlorination being conducted in the apparatus described on p. 2289. On distillation, no fractionation was accomplished, as the whole boiled between 188° and 192°/14 mm. Redistillation yielded a viscid, colourless liquid, b. p. 191—192°/14 mm., in a yield of 60—70% (Found : Cl, 62·7. $C_9H_4OCl_6$ requires Cl, 62·5%). As it was expected that this fraction would prove to be a mixture of the chlorides figured above, it was decided that the best evidence on this point would probably be obtained by the study of the behaviour of the supposed mixture on hydrolysis with chalk and water. The pentachlorinated acid chloride (120 g.) was boiled with excess of chalk and water in the usual manner for 12 hours, when, on cooling and acidifying, a crystalline mass separated immediately; this was filtered off and the filtrate (A) reserved for

further examination. The mass after two recrystallisations from acetic acid, in which it was only sparingly soluble in the cold, melted at 237° and consisted of 2-*aldehydoterephthalic acid*. The melting point was raised to 242° by dissolving in dilute sodium hydroxide and then adding excess of dilute hydrochloric acid; the clear solution, on standing over-night, had deposited long, glistening needles of the pure dibasic aldehydo-acid (Found: C, 55·9; H, 3·2. $C_9H_6O_5$ requires C, 55·7; H, 3·1%). Titration: 0·1636 required for neutralisation 16·8 c.c. of *N*/10-NaOH, whereas this amount of a dibasic acid, $C_9H_6O_5$, should neutralise 16·8 c.c.

The conversion of 2-aldehydoterephthalic acid into the corresponding alcohol and acid by the action of alkalis does not proceed so readily as in the case of 4-aldehydo-1 : 2-phthalide (p. 2279), since it was found necessary to boil with 25% sodium hydroxide to complete the decomposition. On acidifying the cold solution, a colloidal mass separated which was difficult to filter and, on dissolving the mass in boiling alcohol and allowing to cool slowly, a crystalline mass separated which melted at 280° and consisted of 4-*carboxy*-1 : 2-*phthalide*, since a mixed melting point with a specimen of this substance obtained as described on p. 2291 showed no depression.

Anhydro-2-aldehydoterephthalic acid phenylhydrazone,

$$CO_2H\cdot C_6H_3\begin{<}CH{:}N\\CO\cdot NPh\end{>},$$

is obtained by adding phenylhydrazine to the aqueous solution of the acid, and crystallises from alcohol in colourless clusters of prisms, m. p. 326—327°. This high melting point coupled with the absence of colour is in harmony with a derivative of terephthalic acid and the presence of the opiazone ring (Found: C, 68·1; H, 3·9; N, 10·4. $C_{15}H_{10}O_3N_2$ requires C, 67·7; H, 3·8; N, 10·5%). On titration, 0·0730 required 2·8 c.c. of *N*/10-NaOH for neutralisation, whereas this amount of a monobasic acid, $C_{15}H_{10}O_3N_2$, should neutralise 2·74 c.c.

2-*Aldehydoterephthalic Acid Oxime*, $CO_2H\cdot C_6H_3(CH{:}N\cdot OH)\cdot CO_2H$, *and the Imide of Trimellitic Acid*, $CO_2H\cdot C_6H_3\begin{<}CO\\CO\end{>}NH$.—When the aldehydo-acid (0·5 g.) is mixed with a concentrated aqueous solution of hydroxylamine hydrochloride (1 g.) and a little alcohol (3 c.c.), the crystals soon change into a thick precipitate of the oxime, which is difficult to recrystallise but separates from alcohol as a rather indefinitely crystalline powder (Found: C, 51·1; H, 3·6; N, 6·3. $C_9H_7O_5N$ requires C, 51·7; H, 3·3; N, 6·7%). On titration: 0·0839 required 8·2 c.c. of *N*/10-NaOH for neutral-

isation, whereas this amount of a dibasic acid, $C_9H_7O_5N$, should neutralise 8·03 c.c.

This oxime decomposes at about 136° with a slight puff and the melt almost immediately solidifies and melts again at about 242°. The substance so formed crystallises from water in needles, m. p. 248—249°, and has all the properties of the imide of trimellitic acid, a small specimen of which was prepared from trimellitic acid for comparison.

4-Aldehydo-1 : 2-phthalic Acid, $CHO\cdot C_6H_3(CO_2H)\cdot CO_2H$.—The filtrate A (see above) from the 2-aldehydoterephthalic acid was extracted several times with ether and the ether removed, when a colourless, seemingly amorphous residue was obtained which contained 2 : 4-dialdehydobenzoic acid, trimellitic acid, and 4-aldehydophthalic acid. We were unsuccessful in our efforts to obtain the last acid in a state of purity, but it was easily identified by means of the phenylhydrazone. Addition of phenylhydrazine to a dilute acetic acid solution of the mixed acids soon precipitates a mixture of phenylhydrazones, on warming, which are partly soluble in dilute ammonia.

When the mixture was extracted with this reagent, anhydro-2 : 4-dialdehydobenzoic acid diphenylhydrazone (p. 2292) remained undissolved and was filtered off, and the weight of this showed that 2 : 4-dialdehydobenzoic acid must have been present to the extent of 25% of theory calculated on the original chlorinated chloride. The filtrate, on acidifying, deposited a gelatinous mass very difficult to filter and, when this was extracted with boiling water, the filtered extract deposited, on cooling, yellow nodules which melted at 118° and at the same time lost water and turned red. Analysis indicated that this substance is the *hydrate* of the *phenylhydrazone* of *4-aldehydophthalic acid* (Found : C, 60·4; H, 4·7; N, 9·7. $C_{15}H_{12}O_4N_2,H_2O$ requires C, 59·6; H, 4·6; N, 9·3%). If this hydrate is exposed in a vacuum desiccator over sulphuric acid until the weight is constant, the mass melts at 174° with loss of water and is evidently the *phenylhydrazone* of *4-aldehydophthalic acid* (Found : C, 63·4; H, 4·7; N, 9·7. $C_{15}H_{12}O_4N_2$ requires C, 63·4; H, 4·2; N, 9·9%).

When this substance is heated in the air-oven at 115°, it loses a molecule of water and is converted into the corresponding phthalic anhydride, an orange-red powder, m. p. 216—217°, which is not soluble in sodium carbonate (Found : C, 67·1; H, 3·7. $C_{15}H_{10}O_3N_2$ requires C, 67·7; H, 3·8%).

2 : 4-Di(trichloromethyl)benzoyl Chloride, $CCl_3\cdot C_6H_3(CCl_3)\cdot COCl$, *and 2 : 4-Di(trichloromethyl)benzoic Acid*.—The above acid chloride is obtained from 2 : 4-dimethylbenzoyl chloride by introducing 6

chlorine atoms in the usual manner (compare p. 2289) and is a colourless oil, b. p. 192—196°/15 mm., which does not fume in moist air (Found : Cl, 65·2. $C_9H_3OCl_7$ requires Cl, 65·9%). Formic acid does not react with this acid chloride at all readily and, in order to being about hydrolysis and ensure that the decomposition was confined to the acid chloride group, it was found necessary to leave the mixture of the chloride and anhydrous formic acid for about 2 weeks with occasional shaking and warming to, but not above 60°. The solid was collected and recrystallised from petroleum, from which 2 : 4-*di*(*trichloromethyl*)*benzoic acid* separated in colourless needles, m. p. 170—171° (Found : Cl, 58·8. $C_9H_4O_2Cl_6$ requires Cl, 59·6%).

The *anilide*, obtained from the acid chloride by adding aniline to the solution in benzene, separates from alcohol, in which it is sparingly soluble, in colourless prisms, m. p. 202—203° (decomp.) (Found : Cl, 48·9; N, 3·4. $C_{15}H_9ONCl_6$ requires Cl, 49·3; N, 3·3%).

The *amide*, obtained by passing dry ammonia through the acid chloride dissolved in dry benzene, at the laboratory temperature, was collected, washed free from ammonium chloride, and crystallised from benzene, from which it separated in colourless needles which shrank at 165° and melted at 175—176° with evolution of hydrogen chloride (Found : Cl, 59·3. $C_9H_5ONCl_6$ requires Cl, 59·8%).

The *methyl* ester, obtained by boiling the chloride with methyl alcohol, is a thick, colourless liquid, b. p. about 210°/15 mm. Although odourless when cold, it becomes pungent and lachrymatory on warming (Found : Cl, 56·7. $C_{10}H_6O_2Cl_6$ requires Cl, 57·4%). The usual decomposition takes place on heating this ester to boiling and 4-*trichloromethyl*-1 : 2-*phthalyl chloride* is formed, a colourless liquid which distils at 186—187°/12 mm. and has a rather pleasant odour (Found : Cl, 55·6. $C_9H_3O_2Cl_5$ requires Cl, 55·4%). The fact that this substance does not fume in moist air and that it does not appear to be attacked by anhydrous formic acid to yield the corresponding substituted 4-trichloromethylphthalic acid, rather suggests the unsymmetrical formula. On the other hand, the addition of aniline to the solution in benzene causes the separation of a *dianilide* of the probable constitution $CCl_3{\cdot}C_6H_3(CO{\cdot}NHPh)_2$. This separates from alcohol, in which it is only sparingly soluble even on boiling, in minute colourless needles, m. p. 220° (Found : Cl, 24·8; N, 6·5. $C_{21}H_{15}O_2N_2Cl_3$ requires Cl, 24·7; N, 6·5%). It is curious that, whilst 2 : 4-di(trichloromethyl)benzoyl chloride is so resistant to hydrolysis by formic acid, it is readily decomposed by boiling with chalk and water under the usual conditions (p. 2290). On concentrating the solution of the calcium salt and

acidifying with a large excess of hydrochloric acid, trimellitic acid, m. p. 226—227°, is obtained in almost theoretical yield. On titration: 0·05 required 16·0 c.c. of 0·0444 *N*-$Ba(OH)_2$ for neutralisation, whereas this amount of a dibasic acid, $C_9H_6O_6$, should neutralise 16·06 c.c. *The calcium salt.* In one experiment, the concentrated product of the hydrolysis of the hexachlorobenzoyl chloride with chalk was mixed with insufficient hydrochloric acid, when, on standing, a highly characteristic calcium salt separated in feathery needles [Found: Ca, 22·4. $(C_9H_3O_6)_2Ca_3$ requires Ca, 22·4%]. This salt, which does not appear to have been described, is very sparingly soluble in boiling and almost insoluble in cold water.

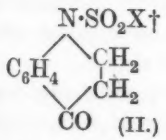
The authors desire to thank the Chemical Society for a grant which has partly covered the cost of this investigation.

THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, July 20th,* 1925.]

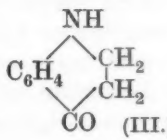
CCCXIV.—*Synthesis of Substituted* 4-*Keto*-1 : 2 : 3 : 4-*tetrahydroquinolines and an Attempt to Synthesise* 4-*Keto*-1 : 2 : 3 : 4-*tetrahydroisoquinoline.*

By GEORGE ROGER CLEMO and WILLIAM HENRY PERKIN, jun.

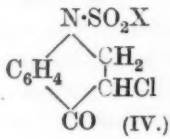
IN the first part of this research (J., 1924, **125**, 1608) it was shown that toluene-*p*-sulphonanilide condenses with β-chloropropionic acid to give the toluene-*p*-sulphonyl derivative of β-anilinopropionic acid, $NPh(SO_2{\cdot}C_6H_4Me){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$ (I) and that this, on treatment with phosphoric oxide, yields the toluene-*p*-sulphonyl derivative of 4-keto-1 : 2 : 3 : 4-tetrahydroquinoline * (II), from which the base itself (III) is obtained on hydrolysis. When, however, (I) is digested with phosphoryl chloride, the toluene-*p*-sulphonyl derivative of 3-chloro-4-ketotetrahydroquinoline (IV) is obtained as the result of combined ring closure and chlorination.



(II.)



(III.)



(IV.)

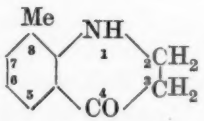
The formation of the chlorinated derivative (IV) and the fact that this is reduced to (III) with elimination of the toluene-*p*-sulphonyl

* Previously named 4-tetrahydroquinolone.

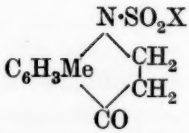
† The abbreviation $-SO_2X$ is used throughout for $-SO_2{\cdot}C_6H_4Me$.

group merely by heating with hydrochloric acid are very difficult to understand. It was mainly with the view of discovering some explanation for this remarkable decomposition that we decided to prepare other cases of a similar kind, and the result of this investigation is described in the present communication. In the first place, the three isomeric *toluene*-p-*sulphonyl*-β-*toluidinopropionic acids* of the type $C_6H_4Me{\cdot}N(SO_2X){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$ were prepared without difficulty from *o*-, *m*-, and *p*-toluidine by a process similar to that described in detail in the former communication. When the *o*-methyl derivative (Ia) was treated with phosphoryl chloride under the conditions previously used in the case of toluene-*p*-sulphonyl-β-anilinopropionic acid (I), a complex mixture was obtained from which a small amount of 4-*keto*-8-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (V; m. p. 92°) was isolated directly, together with a considerable quantity of a substance (VI, m. p. 147°), the analysis of which indicates that it is the toluene-*p*-sulphonyl derivative of (V).

(V.)



(VI.)



(VII.) (*o*)$C_6H_4Me{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4Me$(*o*)

The substance (VI) exhibits very remarkable properties. When it is boiled with a mixture of acetic and hydrochloric acids, it is hydrolysed to *o*-toluidine and β-*o*-toluidinopropionic acid,

$$C_6H_4Me{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H,$$

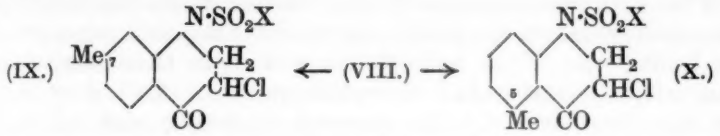
and when treated with concentrated sulphuric acid, (VI) yields β-o-*toluidinopropiono*-o-*toluidide* (VII, m. p. 126°), formed evidently by the condensation of the substances just mentioned, and the constitution of which is demonstrated by the fact that it is produced when the acid chloride of (Ia) is condensed with *o*-toluidine and the product hydrolysed with concentrated sulphuric acid.

If then (VI) represents the constitution of the substance of m. p. 147°, it is clear that, for some reason difficult to understand, scission of the ketotetrahydroquinoline ring must have taken place during the hydrolysis to the substances mentioned above.

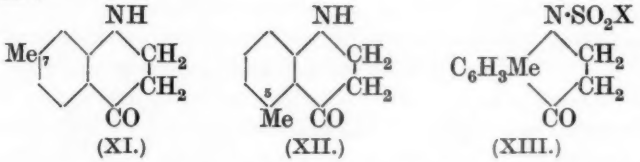
The investigation of the behaviour of *toluene*-p-*sulphonyl*-β-m-*toluidinopropionic acid* (VIII), *m*-$C_6H_4Me{\cdot}N(SO_2X){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, towards phosphoryl chloride has given results very different from those just decribed in the *o*-series.

In these circumstances, this acid behaves like toluene-*p*-sulphonyl-β-anilinopropionic acid (I; see p. 2297), yielding 3-chloro-derivatives, and, as might be expected, ring formation takes place in two

directions with the formation of the substances (IX) and (X) melting at 138° and 100°.



These isomeric *toluene*-p-*sulphonyl*-3-*chloro*-4-*keto*-5- and -7-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinolines* are both hydrolysed and reduced on boiling with hydrochloric acid, yielding 4-*keto*-5- and -7-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinolines* (XI) and (XII) melting at 109° and 105°.

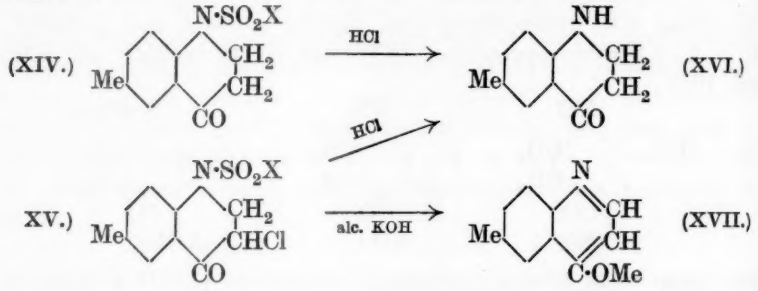


and these yield *toluene*-p-*sulphonyl* derivatives (XIII) melting at 98° and 136° respectively. With regard to the constitutions of these substances derived from *m*-toluidine, there is not sufficient evidence to enable us to assign definitely either formula (IX) or (X) to the toluene-*p*-sulphonyl-3-chloroketomethyltetrahydroquinoline of m. p. 138°. But it is significant that this substance is the main product of the ring closure, being present to the extent of 90% in the product of the action of phosphorus oxychloride on the substituted propionic acid.

In attempting to decide difficult questions of this kind, it must be remembered that ring closure in the benzene ring is, in fact, substitution and therefore the direction of ring closure should follow the rules which govern substitution. The tendency in the present case is probably to close the ring in the *p*-position to the methyl group, the *o*-closure being subsidiary. For this reason, the substance, m. p. 138°, produced in a yield of 90% is presumed to be (IX), in which case the isomeride, m. p. 100°, will be (X). The keto-methyltetrahydroquinoline, m. p. 109°, is then (XI) and the isomeride, m. p. 105°, is (XII). It may be mentioned that this view is borne out by other cases of a similar kind; thus, for example, *m*-toluidine is converted by the Skraup reaction mainly into 7-methylquinoline, and *m*-methoxyphenylhydrazine and acetone yield, by the Fischer synthesis, 6-methoxy-2-methylindole (compare Malkin and Robinson, this vol., p. 370).

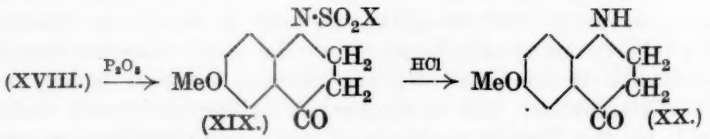
Toluene-p-*sulphonyl*-β-p-*toluidinopropionic acid* (compare p. 2304) was next prepared and its behaviour on treatment with phosphoric

oxide and oxychloride carefully investigated, when it was found that it yielded in the first case *toluene*-p-*sulphonyl*-4-*keto*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XIV), whereas it was converted by the oxychloride into the 3-*chloro*-derivative of this substance (XV). On boiling with dilute hydrochloric acid, both these substances yield 4-*keto*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XVI, m. p. 86°), and the chloro-derivative is converted by boiling with alcoholic potassium hydroxide into 4-*methoxy*-6-*methylquinoline* (XVII, m. p. 51°).



The behaviour of toluene-*p*-sulphonyl-β-*p*-toluidinopropionic acid during the course of this series of changes is therefore exactly similar to that of the corresponding β-anilino-derivative, described in detail in the earlier communication (*loc. cit.*, pp. 1609—1611).

The last series of experiments deals with the formation of methoxy- and ethoxy-derivatives of 4-keto-1 : 2 : 3 : 4-tetrahydroquinoline from *p*-anisidine and *p*-phenetidine, and was undertaken in order to determine whether the methoxy- or ethoxy-group has any considerable influence on the ease with which ketotetrahydroquinoline ring formation takes place. *Toluene*-p-*sulphonyl*-β-p-*anisidinopropionic acid* (XVIII), p-MeO·C_6H_4·N(SO_2X)·CH_2·CH_2·CO_2H, prepared from toluene-*p*-sulphonanisidide and β-chloropropionic acid in the usual manner, yielded on treatment with phosphoric oxide *toluene*-p-*sulphonyl*-6-*methoxy*-4-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XIX), from which 6-*methoxyketotetrahydroquinoline* (XX, m. p. 112°) was obtained by hydrolysis with acids.



That the methoxy-group has an influence on the mechanism of ring closure, different from that exerted by the methyl group, was shown by the behaviour of toluenesulphonylanisidinopropionic acid on

treatment with phosphorus oxychloride, since the product, instead of consisting entirely of *toluene*-p-*sulphonyl*-3-*chloro*-6-*methoxy*-4-*ketotetrahydroquinoline* (compare XV), contained only about 10% of this substance, the remainder consisting of the unchlorinated substance (XIX).

A similar series of observations was made in the case of *toluene*-p-*sulphonyl*-β-p-*phenetidinopropionic acid*,

$$EtO\cdot C_6H_4\cdot N(SO_2X)\cdot CH_2\cdot CH_2\cdot CO_2H\ ;$$

this substance, on treatment with phosphorus pentoxide, yields *toluene*-p-*sulphonyl*-6-*ethoxy*-4-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline*, from which the corresponding *ethoxyketotetrahydroquinoline* (m. p. 60°) is obtained on hydrolysis, whereas treatment with phosphorus oxychloride converts the acid into a mixture consisting mainly of the above toluene-*p*-sulphonyl derivative and containing only a small quantity of the corresponding 3-*chloro*-derivative.

It is interesting that these methoxy- and ethoxy-derivatives may be hydrolysed by hydrochloric acid to the corresponding hydroxy-derivatives; thus 6-methoxy-4-ketotetrahydroquinoline (XX) is converted by hydrochloric acid at 170° into 6-*hydroxy*-4-*ketotetrahydroquinoline*, which crystallises in deep yellow plates, m. p. 164°, and dissolves in sodium carbonate to a deep yellow solution.

The 3-*chloro*-derivatives produced by the action of phosphoryl chloride on toluene-*p*-sulphonyl-β-anilinopropionic acid and its substitution derivatives are readily distinguished from the corresponding unchlorinated substances by the fact that, whereas the former dissolve in strong sulphuric acid with intense violet colorations, hydrogen chloride being evolved, the solutions of the latter are colourless. A quantitative yield of the ketotetrahydroquinoline may be obtained from these colourless solutions, but in the case of the violet solutions the yield is generally only 80%, the remainder consisting of complex substances the nature of which has not been determined.

That these 3-chloro-derivatives should be formed at all under the conditions employed * is very difficult to understand, and that the chlorine atom in the 3-position should be so labile that it is replaced by hydrogen on treatment with hydrochloric acid is apparently without precedent. That the chlorine atom in the group

$$-CO\cdot CHCl\cdot CH_2\cdot N<$$

should be extremely reactive is in accordance with experience, since the bromine atom in the somewhat analogously constituted substance $CH_3\cdot CO\cdot CHBr\cdot CO_2Et$, for example, is readily reduced by cold

* That the formation of these chloro-derivatives is not due to the presence of pentachloride in the oxychloride was proved by experiments conducted with specially purified material.

hydriodic acid, but the only case in which it has been observed that a halogen atom is replaced by hydrogen by the action of hydrogen chloride appears to be that recently recorded by Ridgway and Robinson (J., 1924, **125**, 214), who showed that 8-ethoxy-2-phenylbenzopyrylium chloride is obtained from ethoxysalicylaldehyde and either acetophenone or ω-bromoacetophenone, $C_6H_5\cdot CO\cdot CH_2Br$, by treatment with hydrogen chloride.

During the course of this investigation, attempts were made to obtain derivatives of 4-ketotetrahydro*iso*quinoline corresponding to the 4-ketotetrahydroquinoline derivatives described in the preceding pages. *Toluene*-p-*sulphonbenzylamide* yielded, on condensation with sodium chloroacetate, *toluene*-p-*sulphonylbenzylaminoacetic acid* (m. p. 138°),

$$C_6H_5\cdot CH_2\cdot NH\cdot SO_2X + CH_2Cl\cdot CO_2Na \longrightarrow C_6H_5\cdot CH_2\cdot N(SO_2X)\cdot CH_2\cdot CO_2H \longrightarrow$$

but all attempts to bring about the ring closure sketched above by the action of phosphoric oxide or phosphoryl chloride on the acid or of aluminium chloride on the acid chloride were unsuccessful.

EXPERIMENTAL.

Toluene-p-*sulphonyl*-β-o-*toluidinopropionic Acid*.* — Toluene-*p*-sulphon-*o*-toluidide (52·2 g.) was dissolved by warming in sodium hydroxide (100 c.c. of 8%), a solution of β-chloropropionic acid (22 g.) in sodium hydroxide (100 c.c. of 8%) added, and the mixture gently refluxed for 4 hours, during which some of the sulphon-*o*-toluidide separated as an oil. Water was added and the mixture cooled with stirring until the oily precipitate set to a granular, crystalline mass, which was filtered off, the filtrate acidified, and the colourless gum left over-night, when it had solidified. The solid dissolved completely in hot dilute sodium carbonate but, on cooling, some toluene-*p*-sulphon-*o*-toluidide, which is insoluble in cold sodium carbonate, separated. This was filtered off (total recovered = 27·5 g.), the filtrate acidified, the precipitate, which soon solidified, collected, washed with water, and dried on the steam-bath, when 28·5 g. of almost pure *toluene*-p-*sulphonyl*-β-o-*toluidinopropionic acid* resulted. This acid separated from a little benzene in colourless

* The same molecular quantities and procedure were employed in all the similar condensations described in this communication.

prisms, m. p. 127—128° (Found: C, 61·5; H, 5·7. $C_{17}H_{19}O_4NS$ requires C, 61·3; H, 5·7%).

Action of phosphoryl chloride. The acid (20 g.) was heated with phosphoryl chloride (60 c.c.) at 100° for 15 minutes, the excess of acid chloride removed under reduced pressure, and the gummy residue treated with ice and water and then warmed on the steam-bath for a few minutes. After cooling, the pale yellow aqueous solution was decanted from the gum (A) and made alkaline, when a small amount of a pale yellow solid separated which was collected, dried, and crystallised from light petroleum, from which yellow prisms of 4-*keto*-8-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (V), m. p. 92°, separated (Found: C, 74·7; H, 6·9. $C_{10}H_{11}ON$ requires C, 74·5; H, 6·8%). This substance is readily soluble in acids and also in alcohol or benzene to give solutions which have a green fluorescence. The gum (A) was warmed with dilute sodium carbonate, and after standing, the aqueous layer was decanted from the undissolved material and acidified, when a considerable quantity of toluenesulphonyltoluidinopropionic acid separated. The undissolved substance was crystallised from alcohol, when small prisms of the *toluene*-p-*sulphonyl* derivative of 4-*keto*-8-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (VI), m. p. 147—148°, separated (Found: C, 64·6; H, 5·4. $C_{17}H_{17}O_3NS$ requires C, 64·7; H, 5·4%). When this substance (1 g.) was dissolved in sulphuric acid (5 c.c.), the solution left over-night at the ordinary temperature, and poured on to ice and made slightly alkaline with sodium hydroxide, a colourless substance (about 0·4 g.) separated which crystallised from benzene–ligroin in colourless prisms, m. p. 126° and proved to be β-o-*toluidinopropiono*-o-*toluidide* (VII) (Found: C, 76·0; H, 7·6; N, 10·5. $C_{17}H_{20}ON_2$ requires C, 76·1; H, 7·5; N, 10·4%). The toluene-*p*-sulphonyl derivative of (VII) was synthesised in good yield by treating the acid chloride of toluene-*p*-sulphonyl-β-*o*-toluidinopropionic acid (Ia, from the acid and thionyl chloride) with *o*-toluidine. This substance is hydrolysed by cold concentrated sulphuric acid to give (VII), and boiling with hydrochloric acid converts it into *o*-toluidine and β-*o*-toluidinopropionic acid.

Toluene-p-*sulphonyl*-β-m-*toluidinopropionic Acid* (VIII).—This acid was prepared exactly as described in the case of the isomeric β-*o*-derivative; it dissolves readily in organic solvents and separates from benzene in stout, colourless prisms, m. p. 103° (Found: C, 61·4; H, 5·7. $C_{17}H_{19}O_4NS$ requires C, 61·3; H, 5·7%). The yield was 19 g., and 35 g. of the sulphonyl-*m*-toluidide were recovered.

Action of phosphoryl chloride. Toluene-*p*-sulphonyl-β-*m*-toluidinopropionic acid (VIII; 6 g.) was treated with phosphoryl chloride (20 c.c.) and the product worked up exactly as described in the

case of the corresponding *o*-acid. The substance insoluble in sodium carbonate was dissolved in a little methyl alcohol, when, on cooling, colourless prisms were quickly deposited which, after about 2 hours, were collected (filtrate A) and recrystallised from methyl alcohol, from which the substance separated in well-defined prisms, m. p. 138° (Found: Cl, 10·3. $C_{17}H_{16}O_3NClS$ requires Cl, 10·2%).

Toluene-p-*sulphonyl*-3-*chloro*-4-*keto*-7-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (IX) dissolves in sulphuric acid to an intense violet solution and when hydrolysed with a boiling mixture of acetic and hydrochloric acids (*loc. cit.*, p. 1616) gives an almost quantitative yield of 4-*keto*-7-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XI), which crystallises from benzene–ligroin in bright yellow leaflets, m. p. 109° (Found: C, 74·5; H, 6·8. $C_{10}H_{11}ON$ requires C, 74·5; H, 6·8%).

This substance is readily soluble in alcohol, giving a yellow solution with a pale green fluorescence, and, when treated with toluene-*p*-sulphonyl chloride, the *toluene*-p-*sulphonyl* derivative, *i.e.*, the unchlorinated analogue of (IX), is obtained; this separates from alcohol in rhombic prisms, m. p. 98°, and dissolves in sulphuric acid to an almost colourless solution (Found: N, 4·4. $C_{17}H_{17}O_3NS$ requires N, 4·4%).

The filtrate (A) contained the *toluene*-p-*sulphonyl* derivative of 3-*chloro*-4-*keto*-5-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (X; 0·29 g.) and, on standing, this gradually separated in colourless plates, which were recrystallised from ligroin and melted at 98—100° (Found: Cl, 10·3. $C_{17}H_{16}O_3NClS$ requires Cl, 10·1%). This substance gives the characteristic violet colour with sulphuric acid and is hydrolysed by acids to 4-*keto*-5-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XII), which crystallises from ligroin in long, yellow prisms, m. p. 104—105° (Found: C, 74·8; H, 7·0. $C_{10}H_{11}ON$ requires C, 74·5; N, 6·8%).

The *toluene*-p-*sulphonyl* derivative of this base crystallises from ligroin–benzene in long, almost colourless prisms, m. p. 136°, and dissolves in sulphuric acid without colour.

Toluene-p-*sulphonyl*-β-p-*toluidinopropionic Acid*.—This acid, prepared in the usual manner, separated from benzene in thin, colourless prisms, m. p. 116—117°. When it (6·6 g.) was treated with phosphoric oxide (5·6 g.) and xylene (50 c.c.) (compare *loc. cit.*, p. 1615), *toluene*-p-*sulphonyl*-4-*keto*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XIV) resulted; this separated from alcohol in colourless prisms, m. p. 136—137° (Found: N, 4·3. $C_{17}H_{17}O_3NS$ requires N, 4·4%).

This substance dissolves in sulphuric acid to an almost colourless solution and is hydrolysed by acids quantitatively to 4-*keto*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (see below).

When the β-*p*-acid, m. p. 116—117° (20 g.) was treated with

phosphoryl chloride (60 c.c.) in the usual manner (compare p. 2303), and the product insoluble in sodium carbonate crystallised from alcohol, *toluene*-p-*sulphonyl*-3-*chloro*-4-*keto*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XV) separated in well-defined, colourless, glistening prisms, m. p. 176—177° (Found : Cl, 10·2. $C_{17}H_{16}O_3NClS$ requires Cl, 10·2%).

This substance dissolves in sulphuric acid, with evolution of hydrogen chloride, to an intense purple solution and, on boiling with acetic and hydrochloric acids, undergoes hydrolysis, yielding 4-*keto*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XVI), which crystallises from benzene–ligroin in yellow plates, m. p. 85—86° (Found : C, 74·8; H, 6·8. $C_{10}H_{11}ON$ requires C, 74·5; H, 6·8%). This substance is readily soluble in dilute acids and in most organic solvents, giving the usual green fluorescent solutions. It yields a 3-*benzylidene* derivative, which crystallises from methyl alcohol in thin, yellow prisms, m. p. 224—225° (Found : C, 81·6; H, 5·9. $C_{17}H_{15}ON$ requires C, 81·9; H, 5·6%). This derivative readily combines with two atoms of bromine, and when the dibromide is refluxed with methyl-alcoholic potassium hydroxide, hydrogen bromide is removed and a *monobromo*-derivative is obtained which crystallises from alcohol in stout, colourless prisms, m. p. 194—195°, and gradually dissolves in dilute alkali (Found : C, 62·4; H, 4·4; Br, 24·1. $C_{17}H_{14}ONBr$ requires C, 62·2; H, 4·3; N, 24·4%).

4-*Methoxy*-6-*methylquinoline* (XVII).—The chloro-derivative (20 g.) was refluxed for 16 hours with methyl-alcoholic potassium hydroxide (75 c.c. of 20%), the alcohol removed, water added, the oily base extracted with benzene, dried over potassium hydroxide, and fractionated, when 8 g. passed over at 185°/18 mm. and crystallised; it separated from ligroin (b. p. 60—80°) in needles, m. p. 51° (Found : C, 76·0; H, 6·4. $C_{11}H_{11}ON$ requires C, 76·3; H, 6·3%).

Toluene-p-*sulphonyl*-β-p-*anisidinopropionic Acid* (XVIII).—This acid was prepared from toluene-*p*-sulphonanisidide and β-chloropropionic acid and crystallised from benzene in small, colourless prisms, m. p. 81—82° (Found : C, 58·4; H, 5·5. $C_{17}H_{19}O_5NS$ requires C, 58·5; H, 5·4%). Treated in xylene solution with phosphoric oxide under the conditions described in detail in the previous communication (*loc. cit.*, p. 1616), it yielded *toluene* p-*sulphonyl*-6-*methoxy*-4-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XIX), which separated from alcohol in colourless prisms, m. p. 124—125° (Found : N, 4·3. $C_{17}H_{17}O_4NS$ requires N, 4·2%). This substance dissolves in sulphuric acid to a colourless solution and is hydrolysed by acids to 6-*methoxy*-4-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XX; see below).

When the acid (XVIII) (20 g.) was digested with phosphoryl chloride under the usual conditions, and the product insoluble in sodium carbonate boiled with a little methyl alcohol and filtered from about 0·5 g. of insoluble material (Y), the filtrate deposited 8·5 g. of a substance which, on recrystallisation, separated in colourless prisms, m. p. 115—120°. Analysis indicated that this substance was a mixture of about 90% of the substance (XIX) with about 10% of the corresponding 3-chloro-derivative (compare p. 2300).

When this mixture was hydrolysed with acids, it gave a large yield of *6-methoxy-4-keto-1 : 2 : 3 : 4-tetrahydroquinoline*, which crystallised from benzene–ligroin in bright yellow prisms, m. p. 112° (Found : C, 67·8; H, 6·3. $C_{10}H_{11}O_2N$ requires C, 67·8; H, 6·2%).

This substance is a strong base and dissolves readily in most organic solvents to give deep yellow solutions exhibiting a green fluorescence. The substance (Y), sparingly soluble in alcohol, separates from acetic acid in colourless prisms, m. p. 235° (Found : C, 58·3; H, 4·2; N, 4·2; Cl, 9·8. $C_{17}H_{16}O_3NClS$ requires C, 58·4; H, 4·2; N, 4·0; Cl, 9·2%). This analysis suggests that this substance may be *toluene-p-sulphonyl-3-chloro-6-methoxydihydroquinoline*, but the amount available was too small for further investigation. It dissolves in sulphuric acid to a colourless solution with an intense pale blue fluorescence.

Toluene-p-sulphonyl-β-p-phenetidinopropionic Acid (compare XVIII).—Prepared from toluene-*p*-sulphonphenetidide and β-chloropropionic acid, this acid crystallises best from 75% methyl alcohol, in colourless, well-defined prisms, m. p. 97° (Found : C, 59·8; H, 6·0. $C_{18}H_{21}O_5NS$ requires C, 59·5; H, 5·8%). On treatment with phosphoric oxide, it yields a small amount of *toluene-p-sulphonyl-6-ethoxy-4-keto-1 : 2 : 3 : 4-tetrahydroquinoline*, which separates from methyl alcohol in rectangular prisms, m. p. 114—115° (Found : C, 62·2; H, 5·5. $C_{18}H_{19}O_4NS$ requires C, 62·6; H, 5·5%). This substance gives a colourless solution in sulphuric acid. When the phenetidinopropionic acid was treated with phosphoryl chloride, it yielded a small amount of a substance, m. p. 232°, sparingly soluble in alcohol which clearly corresponds with the substance (Y) described above but was not further examined. The alcoholic filtrate deposited a crystalline substance melting approximately at 100° which was again a mixture consisting mainly of toluene-*p*-sulphonyl-6-ethoxy-4-keto-1 : 2 : 3 : 4-tetrahydroquinoline and containing a small proportion of the corresponding *3-chloro*-derivative. When this mixture was hydrolysed by hydrochloric acid, it yielded *6-ethoxy-4-keto-1 : 2 : 3 : 4-tetrahydroquinoline*, which separated from benzene–ligroin in canary-yellow leaflets, m. p. 60° (Found : C, 69·0; H, 6·9. $C_{11}H_{13}O_2N$ requires C, 69·1; H,

6·8%). This strongly basic substance dissolves in most organic solvents to yellow solutions exhibiting a green fluorescence.

6-Hydroxy-4-keto-1 : 2 : 3 : 4-tetrahydroquinoline.—This substance was obtained when the corresponding methoxy-derivative (XX; 4·5 g.) was heated with concentrated hydrochloric acid (30 c.c.) in a sealed tube at 160—170° for 6 hours. On cooling, the hydrochloride separated as a pale brown, crystalline mass, which was collected, stirred with cold concentrated sodium acetate solution, and the yellow base (3·5 g.) crystallised from xylene, from which it separated in deep yellow plates, m. p. 163—164° (Found : C, 66·6; H, 5·6. $C_9H_9O_2N$ requires C, 66·3; H, 5·5%). This substance is sparingly soluble in benzene, but dissolves readily in alcohol and in aqueous sodium carbonate to deep yellow solutions.

Toluene-p-sulphonylbenzylaminoacetic Acid.—Toluene-*p*-sulphonbenzylamide (J., 1905, **87**, 159; 31·2 g.) was dissolved in hot sodium hydroxide (90 c.c. of 8%), a solution of chloroacetic acid (13 g.) in sodium hydroxide (90 c.c. of 8%) added, and the whole refluxed gently for 48 hours. The mixture was then well cooled, acidified with hydrochloric acid, the colourless solid collected, washed with water, extracted with aqueous sodium carbonate, and the undissolved toluene-*p*-sulphonbenzylamide (26·5 g.) filtered off. The acid (5·5 g.) obtained on acidifying the filtrate crystallised from ligroin in long, hair-like prisms, m. p. 137—138° (Found : C, 59·8; H, 5·3. $C_{16}H_{17}O_4NS$ requires C, 60·2; H, 5·5%). When the solution of this acid in alcohol was saturated with dry hydrogen chloride and refluxed for 24 hours, the *ethyl* ester was obtained; it separated from ligroin in rectangular plates, m. p. 51° (Found : N, 4·0. $C_{18}H_{21}O_4NS$ requires N, 4·0%).

The authors are indebted to the British Dyestuffs Corporation for permission to publish the results of this investigation.

THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, July 20th*, 1925.]

CCCXV.—*Interactions of Tellurium Tetrachloride and Aryl Alkyl Ethers. Part I.*

By GILBERT T. MORGAN and HARRY DUGALD KEITH DREW.

WITH purely aliphatic ethers tellurium tetrachloride combines additively to form unstable hygroscopic compounds of the type $Et_2O,TeCl_4$, but with mixed ethers containing aryl and alkyl radicals substitution takes place with elimination of hydrogen chloride.

These observations were first made by Rust (*Ber.*, 1897, **30**, 2829), who condensed phenetole with tellurium tetrachloride, obtaining a compound which separated in yellow needles melting at 185° to which he ascribed formula I. This result was supported by the preparation and analysis of a series of derivatives and homologues.

(I.) $\left(EtO\text{-}C_6H_4\text{-}\right)_2TeCl_2$ $\left(EtO\text{-}C_6H_4\text{-}\right)_2Te$ (II.)

A few years later (*Annalen*, 1901, **315**, 9), Rohrbaech, in repeating the phenetole condensation, obtained Rust's halogenated compound and reduced it with zinc to a halogen-free substance, yellow plates of m. p. 64°, to which he gave formula II. The assumption that in this condensation tellurium entered the aromatic nucleus was, however, challenged by Lederer (*Ber.*, 1915, **48**, 2049; 1916, **49**, 2532), who prepared both di-*p*-phenetyl telluride (formula II) and its di-*o*-isomeride from tellurium dibromide and the corresponding magnesium aryl halides, $EtO{\cdot}C_6H_4{\cdot}MgI$.

These diaryl tellurides, the constitution of which was not in doubt, differed from the Rust-Rohrbaech product and accordingly Lederer designated the latter as an ethylidene compound with the constitution $\left\{C_6H_4\text{-}O{\cdot}CH(CH_3)\text{-}\right\}_2Te$ (III). He also repeated the Rust-Rohrbaech preparation and obtained the orange-red telluride melting at 64°, thus confirming the previous result. Moreover, he generalised his conclusion by a more complete investigation of the corresponding di-*o*-, *m*-, and *p*-anisyl tellurides, which all differed from the product of the Rust-Rohrbaech preparations with anisole and tellurium tetrachloride.

These seemingly exhaustive investigations appeared to show beyond doubt that tellurium did not enter the aromatic nucleus in the Rust condensation and that isomeric compounds were produced with tellurium attached to the side chain.

However, in preparing the Rust-Rohrbaech product in order to test its possible bactericidal properties we used chloroform as a convenient solvent and obtained a large yield of a substance corresponding in properties with Rust's yellow dichloride. This compound on reduction with alkali metabisulphite was completely transformed to the expected orange-red substance. On testing the solubility of this product in water, it was noticed that the crystals did not melt in the boiling solvent, in which they remained insoluble. Examination of fusibility revealed a melting point of 107° and not 64° as given by Rohrbaech and by Lederer. This compound (IV) and the chloride (V), which gave it by reduction,

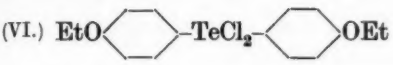
were therefore analysed and found to possess respectively the following molecular formulæ,

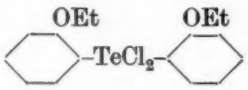
(IV.) $(C_2H_5\cdot O\cdot C_6H_4)_2Te_2$ m. p. 107°. $(C_2H_5\cdot O\cdot C_6H_4)TeCl_3$ (V.) m. p. 183°.

these constitutions being confirmed by the whole of the physical and chemical characteristics of the substances.

Rust and Rohrbaech's formulations for these two substances as diaryl telluride and diaryl tellurium dichloride respectively, although supported by many concordant analyses, are entirely erroneous.

In the course of the present investigation the true dichloride has been prepared and identified. On being heated with more phenetole, the phenetyltellurium trichloride (m. p. 183°) passes into a colourless bisphenetyltellurium dichloride melting at 108°. This compound in all probability is *bis*-p-*phenetyltelluridichloride* (VI), since it melts at 108°, whereas the bis-*o*-phenetyltelluridichloride (VII) prepared by Lederer through the Grignard reaction melts at 163—164°.

(VI.) 



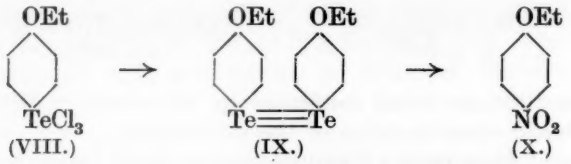
(VII.)

It seems probable that Rust, Rohrbaech, and Lederer were dealing with mixtures of the di- and tri-chlorides and in the case of the last two investigators they also had mixtures of the reduction products of these chloro-derivatives. But it is nevertheless remarkable that the analytical data should agree with those demanded by an incorrect formulation and that the melting point of a compound described as a dichloride, $(EtO\cdot C_6H_4)_2TeCl_2$, should agree with that of the substance now shown to be the trichloride, $EtO\cdot C_6H_4\cdot TeCl_3$.

With our present knowledge of the organic chemistry of tellurium the colour of the products is a useful guide to constitution. Telluridichlorides are invariably colourless and their reduction products are yellowish-white to pale yellow. Telluritrichlorides, on the contrary, are often yellow and their reduction products are intensely coloured (Morgan and Drew, this vol., p. 531).

As further evidence of constitution it was noticed that when the bis-*p*-phenetyl ditelluride was covered with cold concentrated nitric acid and the mixture allowed to evaporate, *p*-nitrophenetole (X) separated, the tellurium being displaced by a nitro-group. This evidence is opposed to Lederer's conclusion as to the attachment of tellurium to the side chain and indicates that the metalloid has entered the para-position with respect to ethoxyl,

thus confirming the following formulæ for p-*phenetyltelluritrichloride* (VIII) and *bis*-p-*phenetyl ditelluride* (IX).



(VIII.) (IX.) (X.)

Lederer's work is defective in another respect. He reduced the Rust-Rohrbaech product from anisole and tellurium tetrachloride, obtaining red needles (m. p. 50°) to which, like Rohrbaech, he assigned a diaryl telluride formula but with tellurium in the side chain, $(C_6H_5{\cdot}O{\cdot}CH_2)_2Te$. On warming this substance with methyl iodide, he obtained a product yielding a picrate alleged to be anisyldimethyltelluronium picrate, $C_6H_2(NO_2)_3{\cdot}O{\cdot}Te(CH_3)_2{\cdot}CH_2{\cdot}O{\cdot}C_6H_5$, one anisyl residue having been eliminated during methylation. The methylation product would accordingly be the iodide, $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}Te(CH_3)_2I$. But actually we find that the supposed "dianisyl telluride," which is in reality bis-*p*-anisyl ditelluride, undergoes on warming with methyl iodide a smooth decomposition into molecular proportions of iodo-derivatives,

$$R{\cdot}Te{:}TeR + 3MeI = RTeMe_2I + RTeMeI_2,$$

where R is the anisyl residue.

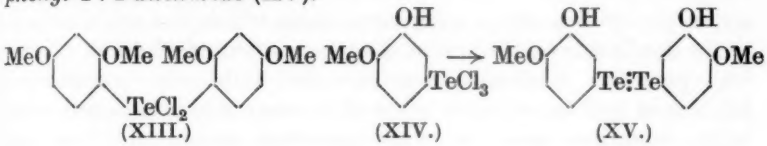
The products are the less soluble p-*anisyldimethyltelluri-iodide*, which gave Lederer his picrate, and the more soluble p-*anisylmethyltelluridi-iodide*, which is easily reduced to p-*anisyl methyl telluride*. Lederer evidently overlooked the more soluble product, and his hypothesis, based on the assumption of an elimination of one of the *p*-anisyl radicals, falls to the ground.

In order to test our conclusions as to the nature of the tellurium tetrachloride condensation with mixed ethers the case of the dimethyl ether of resorcinol was examined. The product was found to be the yellow 1 : 3-*dimethoxyphenyl*-4-*telluritrichloride* (XI), which on reduction furnished the orange-brown *bis*-1 : 3-*dimethoxyphenyl* 4 : 4-*ditelluride* (XII).

When the condensation was forced by heating the reaction mixture with excess of tellurium tetrachloride the tellurium content fell instead of increasing by further substitution in the nucleus; the

product was the colourless *bis*-1 : 3-*dimethoxyphenyl*-4-*telluridichloride* (XIII), while the excess of tetrachloride remained unchanged.

Guaiacol behaves similarly although less smoothly, yielding a 2-*hydroxy*-1-*methoxyphenyl*-4-*telluritrichloride* (XIV), isolated with difficulty but reducing to an orange-brown *bis*-2-*hydroxy*-1-*methoxyphenyl* 4 : 4-*ditelluride* (XV).



(XIII.) (XIV.) (XV.)

EXPERIMENTAL.

Condensation of Tellurium Tetrachloride with Phenetole.

When a mixture of 12 g. of tellurium tetrachloride, 17 g. (3 mols.) of phenetole, and 75 c.c. of dry chloroform was heated under reflux, with exclusion of moist air, during 2 hours, hydrogen chloride was evolved and the solid dissolved. The solution deposited during heating a copious precipitate of glistening, yellow flakes consisting of practically pure p-*phenetyltelluritrichloride* (VIII), which was removed after one day, washed with a little cold chloroform, and dried (yield, 14·5 g. or 92%). This substance was moderately soluble in hot chloroform or benzene to yellow solutions and was readily soluble in cold ethyl alcohol to a solution which was colourless owing to hydrolysis. On warming with aqueous potash the trichloride developed the odour of phenetole. It melted to a red liquid at 182—183° and further crystallisation from dry chloroform resulted in no alteration (Found : Cl, 30·25. $C_8H_9OCl_3Te$ requires Cl, 30·0%).

Bis-p-*phenetyl Ditelluride* (Formula IX).—The foregoing trichloride (6 g.), reduced at 0° with 11·3 g. (3 mols.) of potassium metabisulphite and 50 c.c. of water, gave crude *bis*-p-*phenetyl ditelluride*, in almost quantitative yield, as an orange powder which crystallised from petroleum (b. p. 80—100°) in fluffy masses of brilliant, orange-red needles or golden-orange plates, melting at 107—108° to a deep red liquid. It was readily soluble in cold benzene or chloroform, but much less soluble in light petroleum or ethyl alcohol, and was insoluble in water. Its solutions in organic solvents were red. It was unaffected by boiling aqueous ammonia, but was decomposed by methyl iodide (compare the corresponding *p*-anisyl compound, p. 2314) [Found : C, 38·75; H, 3·4; Te, 51·3; *M*, cryoscopic in benzene, 473 ($c = 1·89$), 481 ($c = 2·92$). $C_{16}H_{18}O_2Te_2$ requires C, 38·6; H, 3·6; Te, 51·3%; *M*, 497].

Although the ditelluride crystallised well from ethyl or methyl alcohol, the product from these solvents was invariably slightly high in carbon content (found: C, 39·25, 39·1; H, 3·7, 3·7), indicating the presence of an impurity which was not completely eliminated by subsequent crystallisation from petroleum. It was noticed, also, that solutions of the ditelluride, when unduly exposed to the air, tended to deposit an amorphous oxide which was again reduced to the ditelluride by the action of aqueous alkali bisulphites. When bis-*p*-phenetyl ditelluride was covered with cold concentrated nitric acid and the solution allowed to evaporate in an open basin, large, colourless spears of *p*-nitrophenetole separated. This substance melted at 60—61° and did not depress the melting point of an authentic specimen of *p*-nitrophenetole (Kahlbaum).

Bis-p-*phenetyltelluridichloride* (Formula VI).—When *p*-phenetyltelluritrichloride was heated with four times its weight of phenetole during 6 hours on an oil-bath at 180—190°, hydrogen chloride was evolved and the addition of petroleum then caused the deposition of *bis*-p-*phenetyltelluridichloride*, which was purified by crystallisation from methyl alcohol. The dichloride formed colourless, glistening, prismatic needles, melting at 108° to a colourless, transparent liquid. In this substance the chlorine was very firmly attached, being only slowly liberated (along with phenetole) even by boiling aqueous potash (Found: C, 43·3; H, 4·0; Cl, 16·1. $C_{16}H_{18}O_2Cl_2Te$ requires C, 43·6; H, 4·1; Cl, 16·1%).

Condensation of Tellurium Tetrachloride with Resorcinol Dimethyl Ether.

Tellurium tetrachloride (2·9 g.), resorcinol dimethyl ether (1·5 g.; 1 mol.), and dry chloroform (30 c.c.), when heated on the water-bath during 2 hours, evolved hydrogen chloride and formed a deep brownish-yellow solution. After removal of the chloroform, a syrup remained which crystallised when it was stirred with a little cold carbon tetrachloride, this solvent poured off, and a little chloroform added. The yellow, crystalline powder (2·7 g.) consisted of crude 1:3-*dimethoxyphenyl*-4-*telluritrichloride* (XI), which was purified by crystallisation from dry chloroform. The trichloride formed silky, primrose-yellow, prismatic needles or transparent, golden-yellow prisms, melting at 155—156° to a yellow liquid which at once became red. On warming with aqueous potash the compound evolved resorcinol dimethyl ether (Found: Cl, 28·8. $C_8H_9O_2Cl_3Te$ requires Cl, 28·7%).

When the proportion of resorcinol dimethyl ether in the foregoing condensation was increased to 2 mols. (4·2 g. of tellurium tetrachloride, 4·2 g. of resorcinol dimethyl ether, and 10 c.c. of dry

chloroform heated on the water-bath during 11 hours), the solid product (4·9 g.) was a mixture of the yellow trichloride and colourless *bis*-1 : 3-*dimethoxyphenyl*-4-*telluridichloride* (XIII). Similarly, when 2 mols. of tellurium tetrachloride and 1 mol. of resorcinol dimethyl ether were employed and a higher temperature was obtained by diminishing the proportion of solvent (6·7 g. of tellurium tetrachloride, 1·8 g. of resorcinol dimethyl ether, and 12 c.c. of dry chloroform heated on the water-bath for 3 hours), a second atom of tellurium was not introduced into the aromatic nucleus; but, instead, a portion of the tellurium tetrachloride remained unchanged and the product consisted of the dichloride admixed with a proportion of trichloride. Reduction with an excess of aqueous potassium metabisulphite led to the destruction of the trichloride, leaving the dichloride unchanged. The latter was extracted from the black reduction product by means of boiling ethyl alcohol, from which it separated on cooling. *Bis*-1 : 3-*dimethoxyphenyl*-4-*telluridichloride* crystallised from alcohol in colourless, pearly flakes which melted without apparent decomposition at 204—205°. It was resistant to the reducing action of aqueous alkali bisulphite, but was decomposed by hot aqueous potash with liberation of resorcinol dimethyl ether (Found : Cl, 14·9. $C_{16}H_{18}O_4Cl_2Te$ requires Cl, 15·0%).

In the above condensations of tellurium tetrachloride with phenetole and with resorcinol dimethyl ether, respectively, the fact that a telluritrichloride is practically the sole product when an excess of the aromatic ether is used in the case of phenetole, but not in that of resorcinol dimethyl ether, seems to be due mainly to the comparative insolubility in chloroform of the telluritrichloride of phenetole. This product is thrown out of solution as formed and in the presence of chloroform is only slowly changed to a dichloride by the further action of another molecule of phenetole.

Bis-1 : 3-*dimethoxyphenyl* 4 : 4-*Ditelluride* (XII).—1 : 3-Dimethoxyphenyl-4-telluritrichloride (1·2 g.), reduced with 2·1 g. of potassium metabisulphite and 10 c.c. of water, was quantitatively transformed to the ditelluride, which was extracted with ether and purified by crystallisation from benzene, petroleum (b. p. 80—100°), or ethyl alcohol. *Bis*-1 : 3-*dimethoxyphenyl* 4 : 4-*ditelluride* separated in orange-brown needles or prisms, a specimen from benzene melting at 134—135° to a deep red liquid. It was insoluble in water, but moderately soluble in ether or ligroin to orange-red solutions. It was unaffected by aqueous alkalis, but gave an intense reddish-purple coloration with cold concentrated sulphuric acid [Found : C, 36·1; H, 3·6 (specimen from benzene) :

C, 37·0; H, 3·5 (specimen from alcohol). $C_{16}H_{18}O_4Te_2$ requires C, 36·3; H, 3·4%].

Condensation of Tellurium Tetrachloride with Guaiacol.

Tellurium tetrachloride (1 mol.) was mixed with guaiacol (2 mols.) and dry chloroform (5 c.c. per g. of tellurium tetrachloride). Hydrogen chloride was evolved and a deep yellowish-green solution was formed on heating during 2½ hours on a water-bath. This solution, concentrated to a syrup in a vacuum desiccator, partly solidified after extraction of unchanged guaiacol by means of petroleum. The greenish-yellow solid was separated by boiling with dry chloroform or benzene into an amorphous, insoluble, mustard-yellow powder decomposing near 180° (not identified) and *2-hydroxy-1-methoxyphenyl-4-telluritrichloride* (XIV), which separated from dry chloroform in transparent, deep yellow prisms, m. p. 157—159° (decomp.). This substance, which was readily hydrolysed by moist air when in solution, was not obtained in a pure condition (Found: Cl, 28·9. $C_7H_7O_2Cl_3Te$ requires Cl, 29·8%).

When reduced with aqueous potassium metabisulphite at 0°, the telluritrichloride was transformed to *bis-2-hydroxy-1-methoxyphenyl 4:4-ditelluride* (XV), which was extracted by means of ether and subsequently purified by crystallisation from dry benzene. The ditelluride formed orange-brown, prismatic needles, slowly darkening above 114° and melting finally at 117—118° with liberation of tellurium. It was sparingly soluble in petroleum, but moderately soluble in benzene, chloroform, or ether, giving red solutions. Boiling ethyl alcohol caused its decomposition. It was insoluble in water, but dissolved in aqueous caustic soda or sodium carbonate (although not in aqueous sodium bicarbonate) to yellowish-orange solutions of the sodium salt, from which the ditelluride was reprecipitated on addition of mineral acids (Found: C, 33·8; H, 2·95. $C_{14}H_{14}O_4Te_2$ requires C, 33·55; H, 2·8%). Addition of chloroacetic acid to a solution of the ditelluride in aqueous caustic soda caused the precipitation of purplish-blue flakes of a substance which soon decomposed when removed from the liquid but was more stable in the form of its red solution in dilute aqueous caustic soda.

Action of Methyl Iodide on Bis-p-anisyl Ditelluride.—The deep red-brown solution of 5 g. of the pure ditelluride (m. p. 56—58°) in 78 g. of pure methyl iodide was heated under reflux on a water-bath for ½ hour, when a microcrystalline, salmon precipitate (4·6 g.) of *p-anisyldimethyltelluri-iodide*, $CH_3{\cdot}O{\cdot}C_6H_4{\cdot}Te(CH_3)_2I$, was thrown down (see equation, p. 2310). This substance melted at 170—172° and was almost insoluble in acetone, benzene, and other organic

solvents, but was hydrolysed by boiling alcohol. It was not reduced by aqueous alkali bisulphites. When warmed with aqueous sodium picrate containing free picric acid, it was decomposed giving two picric acid compounds: (1) Lederer's picrate,

$$CH_3{\cdot}O{\cdot}C_6H_4{\cdot}Te(CH_3)_2{\cdot}O{\cdot}C_6H_2(NO_2)_3,$$

forming bright yellow needles from alcohol or water, m. p. 126—127°; and (2) a substance forming pale yellow, glistening plates from alcohol, which decomposed with effervescence to a transparent, yellow liquid at 176° after changing slowly from about 160°. This substance was probably an additive compound of picric acid and *p*-anisyl methyl telluride, the latter being formed from the above iodide by loss of methyl iodide on heating.

The methyl iodide mother-liquor from the foregoing telluri-iodide contained only p-*anisylmethyltelluridi-iodide*,

$$CH_3{\cdot}O{\cdot}C_6H_4{\cdot}Te(CH_3)I_2$$

(4·7 g.), a red, crystalline substance melting at 109° and soluble in organic solvents (Found: I, 50·1. $C_8H_{10}OI_2Te$ requires I, 50·4%). This substance was readily reduced on shaking with aqueous potassium metabisulphite in presence of ether, with formation of p-*anisyl methyl telluride*, a yellow oil of nauseating odour. Part of the di-iodide, however, was re-transformed to bis-*p*-anisyl ditelluride by partial reduction followed by intramolecular loss of methyl iodide. The reactions occurring may be represented as follows:—

(1) $MeO{\cdot}C_6H_4{\cdot}TeMeI_2 \xrightarrow{2H} 2HI + MeO{\cdot}C_6H_4{\cdot}TeMe.$

(2) $2MeO{\cdot}C_6H_4{\cdot}TeMeI_2 \xrightarrow{2H}$
$2HI + MeO{\cdot}C_6H_4{\cdot}TeMeI{\cdot}TeMeI{\cdot}C_6H_4{\cdot}OMe \longrightarrow 2HI + 2MeI +$
$MeO{\cdot}C_6H_4{\cdot}Te{:}Te{\cdot}C_6H_4{\cdot}OMe.$

The authors desire to express their thanks to the Government Grant Committee of the Royal Society and to the Research Committee of the University of Birmingham for grants which have helped to defray the expense of this investigation.

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[*Received, August 5th*, 1925.]

CCCXVI.—*A New Aspect of the Photochemical Union of Hydrogen and Chlorine.*

By RONALD G. W. NORRISH.

Part I. *A General Theory of the Change.*

ON account of its great interest to the student of chemical kinetics, the photochemical reaction between hydrogen and chlorine has received a very large amount of attention during the past hundred years. In spite of this, no theory which describes the mechanism completely has yet been given, and, indeed, few reactions have proved more difficult to interpret. The results which have accumulated from recent work, however, throw a new light upon the problem, and taken together, enable deductions to be drawn which greatly simplify it. In the present paper, a theory of the process is presented which is claimed completely to describe the mechanism, uniting such diverse phenomena as the effects of desiccation and the induction period in one general explanation. It will be shown that harmony between the various phases of the reaction is attained if we accept the view that the primary photochemical reaction—the dissociation of the chlorine molecule into atoms—takes place at the surface of the vessel, and that a quantitative expression on the basis of the existing theory of Nernst can be built up which is in agreement with the experimental findings of Chapman and his co-workers.

One aspect of the reaction, namely, its extreme deviation from Einstein's law of photochemical equivalence (Bodenstein, *Z. Elektrochem.*, 1913, **19**, 836), has found a simple explanation in the chain theory of Nernst ("Grundlagen der neuen Wärmesatzes," Halle, 1918, p. 133). The primary action of the light is considered to be a dissociation of the chlorine molecules in accordance with simple quantum relations. Subsequent action takes place in the manner shown in the following equations (*a*) and (*b*), both of which may be shown thermodynamically to represent reactions of large affinity.

$$Cl + H_2 = HCl + H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$
$$H + Cl_2 = HCl + Cl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

It will be seen that the absorption of one light quantum, by its generation of two chlorine atoms, can thus originate two chains of reactions which are propagated indefinitely throughout the gaseous mixture by the alternate repetition of reactions (*a*) and (*b*), giving rise to a very large number of hydrogen chloride molecules.

The Rôle of Water in the Reaction.—Before we can apply the chain theory of Nernst to explain the complicated relationships found to

hold good by M. C. C. Chapman, in her quantitative study of the reaction (J., 1923, **123**, 3062), it will be necessary to consider in some detail the bearing of the recent work of Coehn and Jung upon the effects of desiccation on the velocity of hydrogen chloride formation, and an important deduction to which this gives rise. The subject was originally opened by Baker (J., 1894, **65**, 612), who showed that combination of the two gases under extremely dry conditions proceeded only very slowly in sunlight, instead of by explosion. Bodenstein and Dux (*Z. physikal. Chem.*, 1913, **85**, 297), on the other hand, showed definitely that desiccation down to a water vapour pressure of 10^{-3} mm. of mercury produced no effect upon the velocity of combination of the two gases. More recently, Coehn and Jung (*ibid.*, 1924, **110**, 705) have been able to extend the limit of desiccation down to a water vapour pressure of 10^{-7} mm., at which point they found the formation of hydrogen chloride to be suspended. From their results and those of Bodenstein and Dux it is evident that the velocity of hydrogen chloride formation is independent of water vapour pressure, when the latter is increased upwards beyond the limit of 10^{-4} mm. but that below this pressure it gradually falls off to zero. No explanation of these important facts was put forward by Coehn and Jung, but the suggestion is here advanced that they become readily explainable if we draw the deduction that *the primary photochemical reaction requires water as a catalyst and takes place only at the walls of the vessel.*

Modern views of adsorption have led us to the belief that surface affinity is in general neutralised by a single layer of adsorbed molecules, and over their whole range of experimentation we may consider that Bodenstein and Dux were dealing with a glass surface completely saturated with water molecules and therefore offering a reaction surface of constant properties. At water vapour pressures below 10^{-4} mm., with preliminary baking out under a vacuum, this surface layer of molecules is unsaturated, until, at 10^{-7} mm., the surface is practically dry, and the formation of hydrogen chloride is suspended.*

This hypothesis is rendered more probable by some simple calculations relative to Coehn and Jung's conditions of experimentation. Their cylindrical reaction bulbs were 10 c.c. in volume, corresponding to a surface area of about 30 sq. cm. The radius of the water molecule being taken as 2×10^{-8} cm., the number required completely to cover the surface is about 2×10^{16}. The number of water mole-

* This explanation may well apply to other cases of the suspension of reaction between gases on extreme drying, which may be regarded as due, not to the " ultra-dryness " of the gases, but to the removal of the catalytically active water film from the walls of the vessel.

cules filling the bulb at 10^{-4} mm. is about $3{\cdot}5 \times 10^{13}$—about 600 times too small to cover the surface—whilst at 10^{-7} mm. the number is 6×10^{-5} times too small. From Coehn and Jung's account of their work it would appear that their experimental bulbs were left for some time in communication with the source of water vapour pressure before sealing off, so that, while in the former case there would probably be time for a distillation of water vapour to occur sufficient to cover the dried surface of the vessel, there would in a like period only be time to cover one-thousandth of the surface at the lower pressure, and probably even less, since the walls of the communicating tubes also have to be saturated. We may therefore suppose that somewhere in the neighbourhood of 10^{-3} or 10^{-4} mm. of water vapour pressure the moisture film at the surface of the reaction vessel ceases to be saturated, and the velocity of hydrogen chloride formation, in accordance with our hypothesis, begins to fall off at this point.

These considerations lead us to the conclusion that dissociation of the chlorine molecule, which is a necessary preliminary to the starting of the Nernst reaction chains referred to above, must occur through the intermediate formation of a loose complex of chlorine and water at the glass surface. It is possible that a hydrate of the form $\begin{matrix}H\\H\end{matrix}\!>\!O\!<\!\begin{matrix}Cl\\Cl\end{matrix}$ exists in the gaseous phase, and such a compound may also be formed at the surface, but under the latter condition it may well be so weakened structurally by the influence of the surface forces as to render photochemical dissociation of the compound possible at the surface, while impossible in the gaseous phase. Thus we may write :

$$\begin{matrix}H\\H\end{matrix}\!>\!O\!<\!\begin{matrix}Cl\\Cl\end{matrix} = H_2O + 2Cl.$$

As an alternative view, we may suppose that, under the combined influence of the force fields of the glass surface and the water molecules, the chlorine molecule receives an induced polarity which renders it the more easily dissociable (see Norrish, J., 1923, **123**, 3006).* Coehn and Jung (*loc. cit.*) have found, moreover, that when the photochemical reaction between hydrogen and chlorine is promoted by ultra-violet light, extreme desiccation has no influence

* In any case there can be no doubt that chlorine adsorbed at the water film covering a glass surface is much more reactive than gaseous chlorine. This has recently been experimentally demonstrated by the present author in conjunction with Mr. Glyn-Jones for the case of the reaction between ethylene and chlorine. This reaction occurs rapidly at the glass surface, and not at all in the gaseous phase, or on a non-polar and dry paraffin wax surface. Details of this work will be published later.

on the velocity of the reaction, and we may assume that the larger energy quantum here concerned is capable of dissociating the dry gaseous chlorine molecules, so that the primary photochemical reaction can occur in this case in the gaseous phase also.

Confining our attention, however, to the action of visible radiation only, we see that the Nernst reaction centres must first originate at the water film of the surface, with chlorine atoms produced there, and may then travel outward into the gaseous phase, each centre being alternately represented by a hydrogen and a chlorine atom as a result of the endless repetition of reactions (*a*) and (*b*) above. A centre of reaction once started will persist until it meets either another centre or encounters the wall of the vessel. In the former case, the atoms of the two centres will combine with each other; in the latter, reaction will occur between the atoms of the centre and the dissociated chlorine atoms at the surface, or with the water at the surface. Since the partial pressure of reaction centres in the system must be extremely minute, encounters of these with the wall of the vessel will be much more frequent than encounters with one another, so that mutual neutralisation may be assumed negligible compared with neutralisation at the surface.

It would thus appear a reasonable deduction that the primary photochemical reaction—the quantised dissociation of the chlorine molecule—occurs as a surface reaction catalysed by water, and that the reaction centre so started (consisting alternately of atomic hydrogen and chlorine) moves outward into the gaseous phase, being destroyed only when it meets the walls of the vessel, or—much more rarely—another centre.

The Induction Period.

The deductions as to the nature of the primary photochemical reaction set forth above suggest a simple explanation of the induction period on the basis of a surface poisoning by foreign substances. Any impurity capable of combining preferentially with the moisture film at the surface of the reaction vessel should act as a poison to the primary photochemical reaction and inhibit the formation of hydrogen chloride. Burgess and Chapman have shown that small traces of ammonia, or impurities producing ammonia, can give rise to artificial induction periods. Arguing from the strong affinity of ammonia for water, there can be little difficulty in ascribing its action to preferential combination with the moisture film. In Part II of this paper the kinetics of the induction period are studied in more detail, and a quantitative research is described which strongly confirms the present hypothesis.

The Anticatalytic Effect of Oxygen.

It was established independently both by Chapman and McMahon (J., 1909, **95**, 135, 959) and by Bodenstein and Dux (*loc. cit*). that the rate of combination of hydrogen and chlorine is inversely proportional to the oxygen concentration. Thus, keeping the partial pressure of hydrogen and chlorine constant, we may write :

$$d[\mathrm{HCl}]/dt = k/[\mathrm{O_2}].$$

Norrish and Rideal (this vol., p. 787) have confirmed the suggestion of Chapman that at the same time the hydrogen and oxygen gradually unite to form water under the photosensitive action of the chlorine. The relationship found to hold between the velocity of water formation and the concentrations of chlorine and oxygen may be expressed by the formula :

$$d[\mathrm{H_2O}]/dt = k'[\mathrm{Cl_2}][\mathrm{O_2}].$$

This reaction receives a simple explanation by assuming that chlorine molecules throughout the gaseous phase, rendered active by the absorption of a light quantum, can activate oxygen by the transfer of intra-atomic energy on collision. We may assume that a similar deactivation is possible at the surface, and in order to explain completely the anticatalytic effect of hydrogen discovered by M. C. C. Chapman it is necessary to assume that oxygen can deactivate the surface molecules only when it collides simultaneously with a hydrogen molecule. Thus water may be formed by photosensitisation throughout the gaseous phase and at the surface, but it is only the latter process that is to be regarded as connected with the anticatalytic effects of oxygen and hydrogen.

The Kinetics of the Hydrogen–Chlorine Reaction.

These ideas will now be applied to the development of a theoretical expression, connecting the rate of formation of hydrogen chloride with the partial pressures of hydrogen, chlorine, and oxygen in the system, which is in complete agreement with the experimental findings of D. L. Chapman and his school (see especially M. C. C. Chapman, J., 1923, **123**, 3078).

Let the gaseous concentration of the components be represented by square brackets enclosing the corresponding formulæ, and constants by K, k, etc. It will be assumed that the chlorine may be adsorbed at the surface of the water film, the fraction, ϕ, of the total area covered being small compared with unity. Under the influence of the light, the adsorbed chlorine gradually reacts with hydrogen to form reaction centres; when a stationary state has been reached,

$$k_1[\mathrm{Cl_2}] = k_2[\mathrm{H_2}]\phi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Let N be at any moment the number of molecules of photochemically activated chlorine present per sq. cm. of surface. Not all of these are to be regarded as capable of starting reaction chains, but only a small fraction which under a favourable combination of circumstances may be considered as completely dissociated.* All the active chlorine molecules at the surface, however, may be deactivated when simultaneously struck by a hydrogen and an oxygen molecule, with the resulting photosensitive formation of water, and also by thermal degradation of their energy, the number deactivated by these two processes being regarded as large compared with those which react with hydrogen. Equating the rates of activation and deactivation at the surface, we have, therefore, when a stationary state has been reached,

$$k_3 I\phi = k_4 N[H_2][O_2] + k_5 N \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where I represents the intensity of illumination.

Combining equations (1) and (2) and collecting constants,

$$N = K_1 I[Cl_2]/[H_2]([H_2][O_2] + k) \quad . \quad . \quad . \quad . \quad (3)$$

Let s and v be the total surface and the volume of the vessel, and n the number of reaction centres present at any moment per c.c. of the reacting system. The rate of production of centres is, according to hypothesis, proportional to the number of contacts between surface active chlorine molecules and the bombarding hydrogen molecules. Hence

$$dn/dt = k_6 sN[H_2]/v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The reaction centres are destroyed on again meeting the walls of the vessel, the constituent atoms reacting there with the adsorbed atomic chlorine or the water. Hence, the much smaller number of centres destroyed in the gaseous phase being neglected,

$$-dn/dt = k_7 ns/v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where s/v is the surface available per unit of volume. Equating equations (4) and (5) for a stationary state, and combining with equation (3), we obtain

$$n = K_2 I[Cl_2]/[H_2][O_2] + k \quad . \quad . \quad . \quad . \quad (6)$$

Now, for a given reaction centre, let t_1 be the average time required for a hydrogen molecule to react with the chlorine atom, and t_2 the time required for a chlorine molecule to react with the hydrogen atom.

* For instance, the active molecule may pass through a series of vibrations, only one phase of which is equivalent to dissociation from the point of view of the bombarding hydrogen molecules.

Then: $t_1 = a/[H_2]$ and $t_2 = b/[Cl_2]$,

where a and b are constants.

In $(t_1 + t_2)$ seconds two molecules of hydrogen chloride are formed per centre, and the process then repeats itself. From n centres, therefore, $2n/(t_1 + t_2)$ molecules of hydrogen chloride are produced per second,

or $$d[HCl]/dt = 2n/(a/[H_2] + b/[Cl_2]) \quad . \quad . \quad . \quad . \quad (7)$$

Combining equations (6) and (7), we obtain finally:

$$d[HCl]/dt = KI[H_2][Cl_2]^2/([H_2][O_2] + k)(a[Cl_2] + b[H_2]) \quad . \quad (8)$$

This expression is completely satisfactory as a general formula for the description of the results of M. C. C. Chapman (*loc. cit.*), if a and b are regarded as comparable in magnitude, and k as small compared with the product $[H_2][O_2]$, except when $[H_2]$ is very small.

The predictions of this expression may be summarised in a manner parallel to the summary of experimental results given by M. C. C. Chapman (*loc. cit.*, p. 3078), and it will be seen on comparison that there is close agreement between experiment and theory:—

(1) No term for the total pressure of the reacting gases is involved in the expression, and $d[HCl]/dt$ is therefore independent of the total pressure of the gas.

(2) If $[H_2]$ and $[O_2]$ be kept constant,

(a) $d[HCl]/dt \propto [Cl_2]$ when $[H_2]$ is small.

(b) $d[HCl]/dt \propto [Cl_2]^{(2-x)}$ when $[H_2] \doteqdot [Cl_2]$, x being less than unity.

(c) $d[HCl]/dt \propto [Cl_2]^2$ when $[Cl_2]$ is small.

(3) If $[Cl_2]$ and $[O_2]$ be kept constant,

(a) $d[HCl]/dt \propto [H_2]$ when $[H_2]$ is small.

(b) $d[HCl]/dt \propto 1/[H_2]^{1-x}$ when $[Cl_2] \doteqdot [H_2]$, x being comparable with unity.

(c) $d[HCl]/dt \propto 1/[H_2]^{1-x}$ when $[Cl_2]$ is small, x being small compared with unity.

(4) If $[H_2]$ and $[Cl_2]$ be kept constant,

(a) $d[HCl]/dt \propto 1/[O_2]$

except

(b) $d[HCl]/dt = k$ when $[H_2]$ is very small.

Summary.

Recent work by Coehn and Jung has shown that while the rate of combination of hydrogen and chlorine in visible radiation is uninfluenced by desiccation down to a water vapour pressure of 10^{-4} mm., it approaches zero between 10^{-4} and 10^{-7} mm. In

explanation, it is here suggested that the primary photochemical reaction—the dissociation of the chlorine molecule into atoms—occurs only at the water film covering the walls of the vessel and that its rate is uninfluenced while the surface layer of water is saturated, but decreases when this is only partly saturated at low water vapour pressures. The resulting "Nernst chains" must extend outward into the gaseous phase, and be destroyed on again meeting the surface. This hypothesis leads to an expression in full agreement with Chapman's quantitative researches.

Part II. *An Experimental Study of the Mechanism and Nature of the Period of Induction.*

It was early observed by Bunsen and Roscoe in their researches on the photochemical union of hydrogen and chlorine (*Phil. Trans.*, 1857, **147**, 381) that the combination of these two gases is preceded by a period of quiescence during which no reaction occurs. This phenomenon, to which they applied the name "photochemical induction," remained a puzzle to early experimenters, until Burgess and Chapman, in a now classical paper (J., 1906, **89**, 1899), showed it to be due to the inhibiting action of small quantities of ammoniacal impurities present in the water of the insolation vessel.

The explanation suggested by Chapman and McMahon (J., 1909, **95**, 1717; 1910, **97**, 847) was based on the supposed production of small quantities of nitrogen trichloride, by the chlorine from the ammoniacal impurities, and the subsequent oxidation of the hydrogen chloride as it was formed, presumably according to the equation $NCl_3 + 3HCl = NH_3 + 3Cl_2$. Such an explanation suffers from the defect that it puts no limit to the period of induction, for the ammoniacal impurity is repeatedly regenerated, and should therefore *continuously* suspend the formation of hydrogen chloride. It is also extremely difficult to conceive of a minute trace of foreign substance *completely* inhibiting a homogeneous gaseous reaction by secondary reaction with one of the products; at best we should expect a decrease in the velocity of hydrogen chloride formation dependent on the concentration of the nitrogen trichloride in the system.

The later suggestion of Chapman and McMahon (*loc. cit.*), that the activated chlorine molecules are used up in sensitising the reduction of the inhibitor by hydrogen, has been confirmed by Norrish and Rideal (this vol., p. 787) for the case of the anticatalytic effect of oxygen and may well apply in the case of some of the other impurities, *e.g.*, nitrogen peroxide; but it is overstrained if we attempt to explain the complete inhibitory effect of ammonia by its means. The two series of phenomena are quite distinct and cannot

be grouped together. On the one hand, the additions of relatively large quantities of oxygen merely *decrease* the velocity of hydrogen chloride formation in inverse ratio to its concentration, whilst on the other, much smaller quantities of ammonia (as will be evident from the data of this paper) *completely inhibit* the hydrogen–chlorine reaction for a period of time proportional to the quantity of ammonia added. The subsequent hydrogen–chlorine reaction which sets in suddenly at the end of the induction period rapidly reaches a maximum velocity which from the observed Draper effects bears no relation to the original ammonia concentration.

These difficulties led the present author to reject the mechanism suggested by Chapman and McMahon as insufficient, and particularly since the conclusions arrived at in Part I of this paper indicate an alternative explanation which is more in accord with experimental fact. If the deduction that the primary photochemical dissociation of the chlorine occurs at the water film covering the walls of the vessel is accepted, we have a very simple means of explaining the induction period as due to a surface poisoning by preferential adsorption of ammonia derived from these impurities. We may suppose that the ammonia covers the surface, and removes from the sphere of action the water essential to the chlorine dissociation, and that the poison must first be removed by reaction with the illuminated chlorine before the surface can be rendered active.

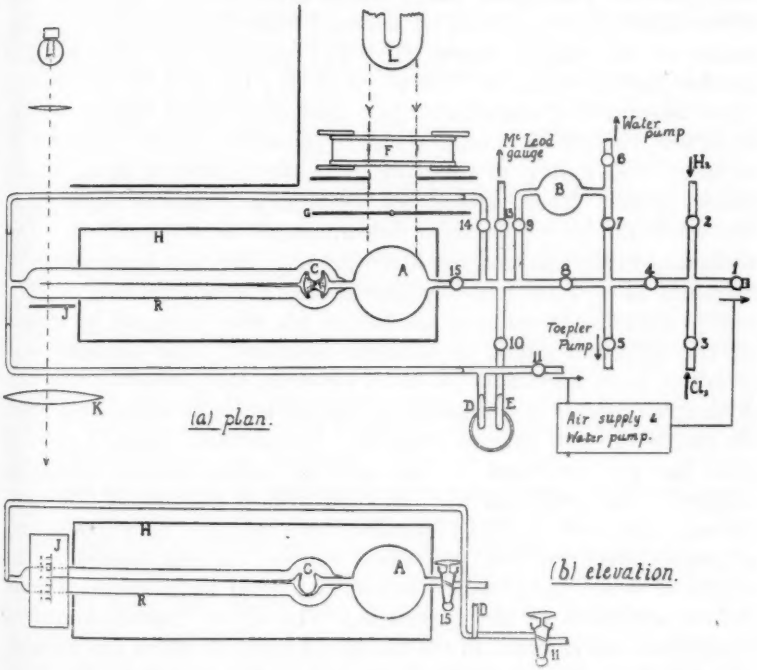
In order to test the likelihood of this view it was necessary to obtain quantitative data relating the induction period to the amount of ammonia, chlorine, and hydrogen in the system, and to the surface extent, and to this end the experimental researches described below were undertaken. The measurements which have been obtained have proved accurately reproducible, and consistent with the hypothesis of surface poisoning advanced above.

In devising an apparatus capable of dealing rapidly and accurately with small quantities of ammonia, it was deemed necessary to dispense with water, present in the insolation vessels of most workers, as absorbent for the hydrogen chloride. As it was only necessary for the present purpose to observe the instant of onset of the hydrogen–chlorine reaction and not its velocity, advantage was taken of the Draper effect or sudden increase of pressure of the gaseous system due to the heat given out when the hydrogen and chlorine start reacting. Another difficulty proved the admission of a small and accurately known amount of ammonia gas to the system. This was eventually solved by making use of the molecular compound of silver chloride and ammonia, $2AgCl,3NH_3$ (Bodländer, *Z. physikal. Chem.*, 1892, **9**, 730), which exerts a known and manageable dissociation pressure of ammonia at the ordinary temperature (Isam-

bert, *Compt. rend.*, 1868, **66**, 1529) and could be used as a source of definite small doses of ammonia.

The apparatus used may be described by reference to Fig. 1. The reaction vessel consisted of a glass bulb (A), of capacity 185 c.c. and diameter 7·0 cm. for most of the experiments described. The reaction chamber was connected on the one hand to the gas supplies and vacuum pumps *via* tap (15), and on the other to an enclosed Bourdon gauge (C). This gauge, which is efficient either as a direct-recording instrument for small pressure changes of from

FIG. 1*a* and 1*b*.



1 mm. to 50 mm., or as a " null " instrument for recording pressures up to one atmosphere, is made by blowing a thin glass bulb of about 7 cm. capacity, attaching a style of glass about 20 cm. long, and then heating in the flame and sucking in one side to the shape shown at (C) in Figs. 1a and 1b. Variation of pressure inside the gauge caused movement of the style, the shadow of which was focussed on a translucent scale (J) and observed through a magnifying glass or telescope (K). The gauge was sealed inside an outer vessel (R), the internal pressure of which could be varied by allowing air to enter or leave by tap (11), and measured by means of the mercury

manometer (D). By equalising the pressures outside and inside the gauge, the pressure of the chlorine gas in A could be measured without the direct use of mercury manometers, which are corroded by the gas. The gauge also proved an accurate and efficient indicator of the small pressure changes due to the Draper effect used as the basis of these measurements.

The source of illumination was a quartz mercury vapour lamp (L) carrying a direct constant current of 3·5 amp. from a 220-volt supply, and placed 20 cm. from the front surface of the bulb (A). The light from the lamp traversed a water cooler (F), with parallel plate-glass sides, which removed the infra-red and ultra-violet rays, and could be screened from the reaction vessel by means of the opaque screen (G). The reaction bulb also and the greater part of the gauge were enclosed in a tin canister as a screen from adventitious radiation. The amount of light falling on the bulb was limited by a hole, 4 cm. in diameter, in the side of this canister, and a stop of the same diameter placed in front of the water cooler. These conditions were kept constant throughout the whole of the comparative measurements to be described. The technique of the chlorine and hydrogen manipulation was essentially the same as that described by Norrish and Rideal (this vol., p. 787), except that the pressure of the former gas was measured by means of the Bourdon gauge as already described. The chlorine was obtained from a cylinder of liquid chlorine, was purified from any hydrogen chloride or ammonia by passage through water, and dried by means of fused calcium chloride. Independent analysis showed that the gas delivered by the cylinder contained no detectable oxygen. The hydrogen was obtained from a cylinder of the compressed gas, and carefully purified from oxygen by passage and repassage over red-hot palladised copper; it was stored in an aspirator over strong soda solution and dried by calcium chloride before admission to the apparatus. The silver chloride–ammonia compound was enclosed in the blackened bulb, B, which was isolated by stopcocks (7) and (9) from the rest of the apparatus and kept filled with pure hydrogen. Definite doses of ammonia could be expanded from B into A by means of the hydrogen gas as carrier. The other connexions of the apparatus are sufficiently evident from the diagram and need no description.

After a preliminary evacuation of the reaction vessel (A) and gauge envelope (R) by means of the water-pumps, the former was exhausted by the Toepler pump until the pressure of the contained air indicated by the McLeod gauge was not greater than 0·05 mm. The pump was then shut off from the apparatus and tap (8) closed. "Ammoniated hydrogen" was then expanded from B into A *via* taps (9) and

(15) until the required pressure, indicated by the mercury manometer (E), was attained. Simultaneously air was allowed to enter the envelope (R) until the same pressure was reached. The bulb (B) was then refilled with hydrogen for later use, by way of taps (2), (4), and (7). After re-evacuation of the connecting tubes, hydrogen to the required pressure registered by the manometer E was expanded into the reaction vessel with the simultaneous admission of air to the gauge envelope, as before. Finally, after the connecting tubes had been again evacuated and "washed out" and the manometer E isolated by tap (10), the chlorine was expanded from its container into the reaction vessel, its pressure being measured by adjusting the style of the gauge to zero on the scale by simultaneously admitting air to the envelope (R).

During this period of gaseous manipulation the lamp had been allowed to reach a steady state of running, the screen (G) being in position. The bulb containing hydrogen, chlorine, and ammonia at known pressures was now exposed to radiation from the lamp, the instant of removal of the screen being noted. The image of the style of the gauge on the illuminated scale was now watched, and readings of its position were made at short intervals. In general, during the induction period the gauge indicator steadily remained at zero, and when this terminated, the onset of the hydrogen–chlorine reaction was marked by a very sudden movement of the style along the scale, as a result of the pressure increase due to the emission of heat by the combining gases. The time from the first instant of illumination to the moment when the first movement of the gauge indicator was observed was noted as the induction period. The increase of pressure rapidly reached a maximum, and continued with a very slow fall as long as the gases were illuminated. If the screen were replaced, the pointer immediately moved back to zero, and on re-illumination the Draper effect *immediately* manifested itself; showing that there is no tendency for the induction period to reappear. A typical graph of these pressure changes is given in Fig. 2 and it will be seen that they are sharp enough to enable the induction period to be obtained to a high degree of accuracy. Its termination could usually be marked to a second or so by means of a stop-watch.

No control of the temperature was included in the apparatus, and was purposely omitted, since water cooling tends to minimise the Draper effect, which is required to be as large as possible for the accuracy of these measurements. The loss of accuracy by this omission is probably very small, since it is well known that photochemical reactions are in general little affected by small changes of temperature. In any case, the temperature of the room rarely

varied from 17° by more than one degree. The temperature of the bulb B was always recorded and from a knowledge of the dissociation pressure of the silver chloride–ammonia compound, and the amount of hydrogen expanded from B into A, the quantity of ammonia carried into the reaction chamber could be calculated.

In Tables I, II, and III are given the results of measurement of the induction period under standardised conditions.

(*a*) Varying the ammonia pressure and keeping the pressure of hydrogen and chlorine constant.

(*b*) Varying the hydrogen pressure, and keeping that of the chlorine and ammonia constant.

(*c*) Varying the chlorine pressure and keeping that of the ammonia constant.*

FIG. 2.

Pressure changes on illumination, showing induction period.

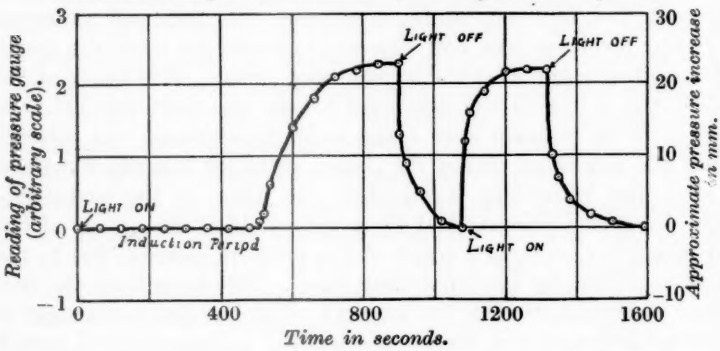


TABLE I.

Variation of Induction Period with Pressure of Ammonia.

Total pressure of hydrogen 160—170 mm.
Total pressure of chlorine 470—490 mm.

x = pressure of "ammoniated hydrogen" admitted to reaction vessel in mm. of Hg; p, the pressure of ammonia in mm. of Hg, $= x \times 0{\cdot}0116$ (correct to 0·05 mm. of Hg); T = induction period in seconds.

x.	p.	T.	$(T/p) \times 10^{-2}$.	x.	p.	T.	$(T/p) \times 10^{-2}$.
0	0	0	—	102	1·30	510	3·9
11	0·15	60	4·0	124	1·45	570	3·9
13	0·15	55	3·7	149	1·75	710	4·1
30	0·35	145	4·1	166	1·95	925	4·7
30	0·35	135	3·9	167	1·95	820	4·2
55	0·65	250	3·8				Mean 4·02
82	0·95	375	4·0				

* It was unnecessary to keep the hydrogen pressure constant in this series, since, as will be seen from Table II, its variation has no effect upon the period of induction.

TABLE II.

Effect of Hydrogen Pressure on the Induction Period.

Pressure of ammonia 0·35 mm. of Hg.
Pressure of chlorine 195—210 mm. of Hg.

Pressure of hydrogen in mm. of Hg	75	117	149	200	300	410	466
Induction period in seconds	180	188	170	165	180	170	180

TABLE III.

Pressure of ammonia 0·35 mm. of Hg.

Pressure of chlorine in mm. of Hg.	Induction period in seconds. Obs.	Calc. $T = 90\,(1 + 200/P)$.	Pressure in chlorine in mm. of Hg.	Induction period in seconds. Obs.	Calc. $T = 90\,(1 + 200/P)$.
46	540	481	235	160	167
49	420	459	272	140	156
73	348	338	314	150	148
105	250	262	372	135	138
146	225	213	402	136	136
208	170	177	481	135	128

It will be seen from these results and the corresponding curves in Figs. 3 and 4 that the length of the induction period is (*a*) directly proportional to the pressure of ammonia, (*b*) independent of the hydrogen pressure, and (*c*) increased at first slowly and later more rapidly as the pressure of the chlorine is decreased.

These results are not consistent with the view of Chapman and McMahon that the ammonia or its derivatives are removed from the system by the hydrogen chloride as it is formed, since the rate of production of the latter is dependent on the hydrogen pressure, while, according to (*c*) above, the induction period is independent of the hydrogen pressure. On the other hand, they do accord with the hypothesis that the ammonia is removed by reaction with the chlorine, which could occur according to the following equations :

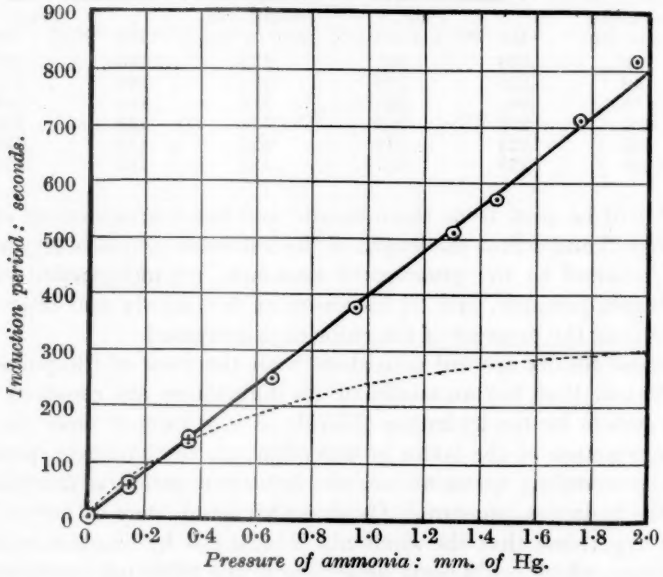
$$2NH_3 + 3Cl_2 = N_2 + 6HCl.$$
$$6HCl + 6NH_3 = 6NH_4Cl.$$

The production of ammonium chloride in the bulb was indeed confirmed by the analysis of an easily sublimable, white deposit which formed on the walls of the reaction chamber when it was used several times successively with high ammonia pressures. This deposit could easily be removed by warming the bulb and washing it out several times with air. A very dilute solution of the deposit in water gave a precipitate with Nessler's solution and a turbidity with silver nitrate, proving it to be ammonium chloride.

The results set forth in Figs. 3 and 4 cannot, however, be interpreted as due to a *homogeneous gaseous* reaction between the chlorine and ammonia, but are in agreement with the view that this reaction occurs on the illuminated surface of the vessel. Thus, in the presence of a large constant excess of chlorine, a homogeneous gaseous reaction would be unimolecular with respect to the ammonia, and the induction period, corresponding with the time required to remove the ammonia, would vary according to the dotted curve shown in Fig. 3; moreover, for constant pressures of ammonia, the induction period should vary in inverse ratio to the chlorine pressure, which is not found to be the case.

FIG. 3.

Variation of induction period with ammonia pressure.



On the other hand, if it is assumed that the surface is at all times saturated with respect to ammonia, and that this is removed by reaction with the bombarding chlorine molecules under the influence of the light, a simple explanation is afforded of the above data. Let the whole surface water film, of area s, be covered with ammonia, and let a fraction, θ, at any moment be reacting with chlorine. The rate of evaporation of the products of this reaction will be proportional to this area, and may be written $\nu\theta s$, where ν is constant. The rate of reaction of chlorine will be proportional to the pressure of the chlorine (P) (*i.e.*, number of collisions with the surface per second) and to the disengaged ammonia surface, $(1 - \theta)\, s$. When

a steady state has set in at the surface, the rate of reaction between the ammonia and chlorine will equal the rate of evaporation of the products, and we may write therefore

$$\nu\theta s = kP(1 - \theta)s,$$

k being constant.

Whence $$\theta = kP/(\nu + kP).$$

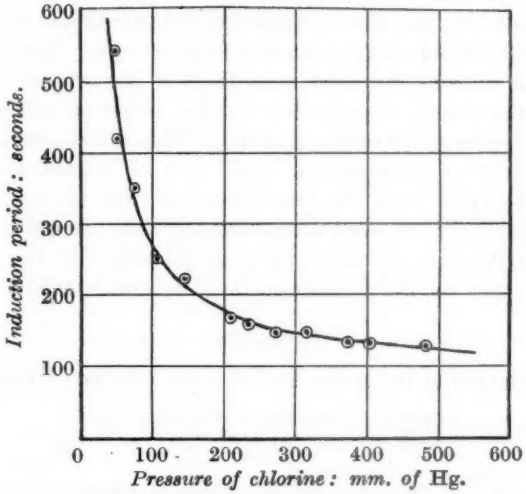
Hence the rate of destruction of the ammonia is

$$r = \nu\theta s = \nu kPs/(\nu + kP).$$

Let p be the pressure of ammonia introduced into the reaction vessel of volume v. Then the total quantity of ammonia to be removed

FIG. 4.

Variation of induction period with pressure of chlorine.



by this surface mechanism is measured by pv, and the time required is the induction period, T.

Hence $$T = pv/r = pv(\nu + kP)/s\nu kP.$$

Writing $1/\nu = a$ and $\nu/k = b$, we obtain $T = apv(1 + b/P)/s$.

If P, the pressure of the chlorine, and the illuminated surface, s, be maintained constant, we have the linear relationship between the initial pressure of ammonia and the induction period obtained experimentally and shown in Fig. 3.

If, on the other hand, the pressure of ammonia, p, and the illuminated surface be maintained constant, then the induction period depends on the chlorine pressure according to the relationship

$$T = k(1 + b/P).$$

Expressing T in seconds, and P in mm. of mercury, and giving to k and b the values 90 and 200 respectively, the curve of this equation has been plotted in Fig. 4; it will be seen that the deviation of the experimental points is in all cases small. The values for the induction period calculated according to this expression are also tabulated in the third column of Table III.

Finally, the formula for the induction period involves no term dependent on the hydrogen pressure, in conformity with the data of Table II.

As a final and crucial test of the expression developed above, it remained to show that the induction period is dependent on the volume of the reaction vessel and the extent of illuminated surface, by a suitable variation of the dimensions of the vessel A.

It will be seen that for constant pressures of chlorine $T/p \propto v/s$. A second bulb was therefore prepared of volume 45 c.c. and diameter 4·4 cm., and interchanged with the original one. The dimensions of the stops limiting the light were kept at the original magnitude (4 cm. in diameter), so that the change in the dimensions of the illuminated surface was relatively small. This was deemed necessary, since the field of illumination could not be considered uniform. Comparative runs with the two bulbs, as will be seen from the results of Table IV, showed unmistakably that the quotient Induction period/Pressure of ammonia is proportional to the volume of the vessel, when the illuminated surface s is kept constant.

TABLE IV.

Variation of Induction Period with Volume of Vessel.

Pressure of chlorine *ca.* 480 mm. of Hg.
Pressure of hydrogen 150—170 mm. of Hg.

Volume of vessel plus gauge (5 c.c.) = v c.c.	Pressure of ammonia, p, in mm. of Hg.	Induction period, T, in secs.	T/p.
50	1·77	180	1·02
	1·96	180	0·92
	1·78	185	1·04
		Mean value	1·00
190	See Table I.	Mean value	4·02

Thus the ratio of the volumes of the two bulbs is $190/50 = 3{\cdot}8$, whilst the ratio of the quotients T/p is $4{\cdot}02/1{\cdot}00 = 4{\cdot}02$, a sufficiently close agreement.

As a means of keeping the volume constant and varying the surface, a bulb containing glass wool was prepared, of 200 c.c. free space. The illuminated surface, limited by the same stops as previously, was in this way augmented by the irregular surface of the glass wool immediately in contact with the front face of the

bulb, and though the back face of the bulb now received no light, the total illuminated surface was considerably in excess of the surface of the bulb containing no glass wool. In spite of the fact that all the ammonia had now to diffuse to the forward surface of the bulb, through the interstices of the obstructing mass of glass wool, the induction period was markedly shortened, the quotient T/p being reduced from 4 to 3, as is shown by the results set out in Table V.

TABLE V.

Variation of Induction Period with Surface of Vessel.

Pressure of chlorine *ca.* 480 mm. of Hg.
Pressure of hydrogen *ca.* 160 mm. of Hg.

Reaction vessel.	Ammonia pressure, p, in mm. of Hg.	Induction period. T (secs.).	$T/p \times 10^{-2}$.
Original (volume 190 c.c.)	See Table I.		Mean value 4·02
Surface increased by glass wool (volume 205 c.c.).	2·0	600	3·00
	2·1	590	2·82
	2·1	620	2·95

These results (Tables IV and V) therefore show (other things being equal) that the induction period is (quantitatively) proportional to the volume of the reaction vessel and (qualitatively) inversely proportional to the illuminated surface, as required by the "surface poisoning hypothesis" developed in this paper. It would indeed be difficult to escape from the view, even if the evidence given in Part I were not available, that the sudden onset of the hydrogen–chlorine reaction, at the termination of the induction period, is due to the liberation of the illuminated surface from the adsorbed ammonia, and its consequent activation for the primary photochemical reaction of the hydrogen–chlorine system.

Summary.

The view developed in Part I is extended to account for the phenomenon of photochemical induction as a surface poisoning effect by ammonia derived from traces of nitrogenous impurities. Ammonia is assumed preferentially to combine with the catalytically active water film, and to require removal by photochemical reaction with the chlorine before the primary reaction can occur.

A quantitative study of the induction period, produced by adding known doses of ammonia to the hydrogen–chlorine system, has been undertaken. The results can be expressed by the formula

$$T = apv(1 - b/P)/s,$$

where T is the induction period, p, P are the pressures of ammonia

and chlorine, v and s are the volume and surface of the reaction vessel, and a and b are constants; and are consistent with the surface poisoning theory set out above.

The author desires to thank the Department of Scientific and Industrial Research for a maintenance grant which has made this work possible.

DEPARTMENT OF PHYSICAL CHEMISTRY,
CAMBRIDGE UNIVERSITY. [*Received, June 17th*, 1925.]

CCCXVII.—*Selective Solvent Action. Part IV. Cryoscopy in Mixed Solvents.*

By ROBERT WRIGHT.

THE depression of the freezing point of a solvent produced by the addition of a solute may be diminished by the subsequent addition of a third substance; the diminution may be due to various causes based on the decrease in the concentration of the solute molecules or complexes in the solution.

In recent papers (J., 1922, **121**, 2252; 1923, **123**, 2493; 1924, **125**, 2068) dealing with the partial vapour pressures of aqueous alcohol, it has been shown that a substance soluble in only one constituent of the aqueous alcohol will, when added to the mixed solvent, lower the vapour pressure of the constituent in which it is soluble and raise the vapour pressure of the other. The formation of solvates would account for this behaviour. Similar results might be expected from a study of the freezing points of such systems. Mihaly (*Z. physikal. Chem.*, 1897, **24**, 13) observed that the addition of water to the mixed solvents alcohol–benzene, phenol–benzene, and acetic acid–benzene raised the freezing point of the benzene, and attributed the results to the formation of hydrates. A cryoscopic examination was therefore made of a considerable number of semi-solutes in the mixed solvents named in Table I (alcohol–water gave indefinite freezing points). As a rule, no difficulty was found in determining the freezing points to 0·02° by the ordinary Beckmann method.

As anticipated, the freezing point of the constituent in which the semi-solute is insoluble is always raised by the addition of the semi-solute. When the concentration of the latter is plotted against the elevation of the freezing point a continuous curve results with a break at the point of formation of two liquid phases.

The insolubility of the solutes in the first constituent of the mixed solvent was tested by noting the effect of excess of the solute on

TABLE I.

Nicotine–Water.

40 C.c. of nicotine in 100 c.c. of water. Density 1·007. F. p. of solution −2°. 20 C.c. of solution used as solvent.

w = wt. in g. of the third substance and $e°$ = elevation of the f. p.

Benzene : w	0·0770	0·1385	0·2130*	0·2977	0·3185	
$e°$	0·030	0·048	0·072	0·081	0·083	
Carbon tetrachloride :						
w	0·0965	0·2020	0·2985*	0·3995	0·5250	
$e°$	0·010	0·022	0·027	0·030	0·031	
Chloroform : w	0·0795	0·1640	0·3020	0·4070*	0·5220	0·6535
$e°$	0·023	0·036	0·075	0·095	0·115	0·126
Methyl salicylate : w	0·0655	0·1430	0·2145	0·2955*	0·3920	0·5070
$e°$	0·043	0·063	0·108	0·125	0·125	0·125
Monobromonaphthalene :						
w	0·0460	0·0975*	0·1375	0·1780	0·2170	
$e°$	0·045	0·060	0·068	0·070	0·070	

Alcohol–Benzene.

25 C.c. of alcohol in 100 c.c. of benzene. Density 0·853. F. p. of benzene 5·5°. F. p. of solution 1·3°. 20 C.c. of solution used as solvent.

Citric acid : w	0·0220	0·0330	0·0445	0·0625	0·1035	excess
$e°$	0·060	0·100	0·145	0·180	0·250	0·770
Tartaric acid : w	0·0130	0·0350	0·0495	0·0667	0·0870	excess
$e°$	0·030	0·090	0·118	0·155	0·197	0·367
Oxalic acid : w	0·0280	0·0590	0·0880	0·1235	0·1550	excess
$e°$	0·065	0·135	0·200	0·295	0·355	2·100
Cadmium iodide : w	0·0482	0·1132	0·2027	0·3092	0·4127	excess
$e°$	0·042	0·083	0·125	0·190	0·252	1·105

Acetone–Benzene.

20 C.c. of acetone in 100 c.c. of benzene. Density 0·856. F. p. of solution −6·2°. 20 C.c. of solution used as solvent.

Mercuric chloride : w	0·1375	0·2035	0·3245	0·4370	excess
$e°$	0·130	0·200	0·290	0·420	0·920
Cadmium iodide : w	0·0730	excess			
$e°$	0·110	0·480			

Alcohol–Ethylene Dibromide.

25 C.c. of alcohol in 100 c.c. of ethylene dibromide. Density 1·888. F. p. of ethylene dibromide 9·5°. F. p. of solution 5°. 20 C.c. of solution used as solvent.

Oxalic acid : w	0·0938	0·1561	0·2298	0·3073	0·4083	0·5028*	0·6001
$e°$	0·175	0·298	0·448	0·610	0·795	0·970	1·115
w	0·7555	0·9523	1·1182	excess			
$e°$	1·375	1·615	1·755	2·080			
Citric acid : w	0·1140	0·2032	0·2875	0·4058	0·6365*	excess	
$e°$	0·170	0·275	0·410	0·590	0·830	1·030	
Tartaric acid : w	0·1060	0·1805	0·3360	excess			
$e°$	0·160	0·260	0·440	0·480			
Water : w	0·0710	0·1365*	0·2335	0·3025	0·4005	0·4830	0·6510
$e°$	0·250	0·510	0·780	0·950	1·110	1·210	1·470

* System separates into two liquid phases.

the freezing point of the pure constituent. Thus excess of water lowered the freezing point of ethylene dibromide by 0·08° and mercuric chloride lowered the freezing point of benzene by 0·05°. The effect produced by all other solutes was less than 0·02°.

It thus seems evident that a semi-solute when dissolved in a mixed solvent forms solvates with the constituent in which it is soluble, and as a result raises both the freezing point and the vapour pressure of the other constituent. Thus the addition of alcohol to benzene lowers the freezing point of the latter and—on the solvate theory—forms alcohol–benzene complexes. The subsequent addition of water decomposes some of these with the formation of water–alcohol complexes; benzene is thus liberated and a more dilute solution with a higher freezing point is produced.

An attempt was made to carry the investigation a step further by adding glucose to the homogeneous solvent consisting of 10 c.c. of benzene, 10 c.c. of alcohol, and 2 c.c. of water, but the results obtained were too indefinite to be of any value.

The effect of solutes soluble in both constituents of a mixture of equal weights of alcohol and benzene was also examined. The solutes used were acetanilide (11), benzoic acid (4), picric acid (0·8), naphthalene (0·3), and phenanthrene (0·08). The figures after each substance indicate roughly the ratio of its solubility in alcohol to that in benzene.

Table II shows that the solutes which are more soluble in alcohol at first raise the freezing point of the benzene and afterwards, at higher concentrations of solute, depress it; whilst those substances which are more soluble in benzene than in alcohol depress the freezing point of the benzene at all concentrations. This may be explained by the view that the substances more soluble in alcohol form solvates with the alcohol more readily than with the benzene, and only at higher concentrations, where the alcohol is to some extent bound, does the depression of the freezing point of the benzene take place. On the other hand, substances more soluble in benzene naturally depress the freezing point in all concentrations.

If it may be concluded from the above results that a substance which at first raises the freezing point of the benzene in the 50% alcohol–benzene mixture and then depresses it is more soluble in alcohol than benzene, whilst a substance which, even in low concentration, depresses the freezing point of the benzene is more soluble in it than in the alcohol; then the method may be applied to discriminate between the relative attractions of benzene and alcohol for a third liquid which is completely miscible with both. Thus if acetic acid has a greater attraction for alcohol than benzene, it will at low concentrations raise the freezing point of the benzene in the

Table II.

Changes in the freezing point of benzene in a 50% (by weight) alcohol–benzene mixture produced by solutes soluble in both constituents of the solvent. F. p. of solution −5·5°. 20 C.c. of solution used as solvent.

w = wt. in g. of the third substance and e = elevation of the f. p.

Acetanilide.		Benzoic acid.		Naphthalene.	
w.	*e.*	*w.*	*e.*	*w.*	*e.*
0·0125	0·09°	0·0475	0·03°	0·0885	−0·18°
0·0268	0·18	0·1065	0·03	0·2130	−0·50
0·0420	0·20	0·2190	−0·06	0·3740	−1·11
0·0767	0·23	0·3545	−0·33		
0·1135	0·38	0·4870	−0·47	Phenanthrene.	
0·1660	0·28			0·0335	−0·07
0·2300	0·18	Picric acid.		0·0647	−0·10
0·3145	0·13	0·0805	−0·04	0·1170	−0·30
0·4090	0·06	0·1775	−0·16	0·2145	−0·51
0·5620	−0·03	0·3255	−0·38	0·3100	−0·73
0·7030	−0·14	0·5045	−0·53		
		0·6900	−0·83		

Changes in the freezing point of benzene in a 50% (by weight) alcohol–benzene mixture produced by solutes completely miscible with each constituent of the mixture. 20 C.c. of the solution used as solvent.

Methyl alcohol.		Propyl alcohol.		*iso*Butyl alcohol.		*tert.*-Amyl alcohol.	
w.	*e.*	*w.*	*e.*	*w.*	*e.*	*w.*	*e.*
0·0450	0·07°	0·0570	0·06°	0·0300	0·13°	0·0420	0·00°
0·0905	0·17	0·1250	0·05	0·0650	0·10	0·0740	0·00
0·1490	0·16	0·2235	0·01	0·1110	0·06	0·1070	0·00
0·2215	0·18	0·4020	−0·19	0·1740	0·04	0·1490	−0·02
0·3250	0·17	0·6160	−0·46	0·2715	0·03	0·2185	−0·09
0·4740	0·01			0·3960	−0·04	0·2950	−0·09
0·5780	−0·17					0·3930	−0·08
0·7780	−0·25					0·5530	−0·14
						0·6710	−0·24
						0·8720	−0·38

n-Heptyl alcohol.		Octyl alcohol.		Acetic acid.		Propionic acid.	
0·0315	0·00	0·0375	−0·02	0·0385	0·00	0·0400	−0·01
0·0655	0·00	0·0810	−0·04	0·0955	0·00	0·0860	−0·07
0·1130	−0·09	0·1405	−0·06	0·1770	−0·17	0·1770	−0·09
0·1780	−0·17	0·2120	−0·14				
0·2840	−0·30						

Butyric acid.		Toluene.		Ethylbenzene.		Nitrobenzene.	
0·0415	−0·02	0·0570	−0·20	0·0442	−0·23	0·0630	−0·12
0·0890	−0·02	0·1100	−0·38	0·1432	−0·66	0·1170	−0·19
0·1845	−0·08	0·1690	−0·76	0·2272	−1·03	0·2650	−0·35
0·3450	−0·36						

Aniline.		Benzyl alcohol.		Phenylethyl alcohol.		Carbon tetrachloride.	
0·0565	−0·03	0·0555	−0·06	0·0505	−0·06	0·0650	−0·06
0·1345	−0·11	0·1310	−0·11	0·1225	−0·14	0·1260	−0·13
0·2295	−0·23	0·2450	−0·23	0·2640	−0·28	0·2425	−0·28

50% mixture, but if the acid has a greater attraction for the benzene it will lower its freezing point at all concentrations.

The results are tabulated for sixteen miscible solutes and it will be seen that the lower members of the fatty alcohol series show a

greater attraction for ethyl alcohol than for benzene. Amyl alcohol up to a considerable concentration has little effect on the freezing point of benzene in the mixed solvent and may therefore be considered to have almost equal attractions for the two constituents. On the other hand, the higher alcohols and the aromatic compounds in general all seem to show a greater attraction for benzene than for alcohol.

A similar phenomenon is met with when a solute is distributed between two liquids with both of which the solute is miscible. Thus acetic acid is miscible both with water and with benzene, but measurements of the partition coefficient show that the acid is much more strongly attracted by the water than by the benzene. The same results are obtained when the acid is partitioned between water and carbon tetrachloride or water and toluene. Miscibility might therefore be considered rather as indefinite than infinite solubility.

The mixed solvent was prepared from equal weights of the two constituents. The usual method of freezing-point determinations was employed, but owing to the great concentration of the alcohol in the 50% mixture the results are not very accurate, though there was little difficulty in getting readings to within 0·05°. The results, however, are only of a qualitative nature and great accuracy is not claimed for them.

GLASGOW UNIVERSITY. [*Received, July 15th,* 1925.]

CCCXVIII.—*Colour and Molecular Geometry. Part IV. Explanation of the Colours of the Cyanine Dyes.*

By JAMES MOIR.

THE conception (this vol., p. 968) that the height of colour depends in the majority of cases mainly on the distance between two positive centres in the molecule may be applied to all classes of coloured substances. In many familiar commercial dyes, however, the molecule contains extensive inactive parts, lying outside the two positive centres. These inactive parts produce a "loading" effect on the colour, raising the position of the absorption band by an amount varying between ½ and 10%. The cyanines, *iso*cyanines, *ψ-iso*cyanines, azocyanines, and carbocyanines belong to this class. Before any explanation of their colours can be attempted it is necessary to estimate in quantitative terms the effect of the "load." This would have been unnecessary if all the parent substances had been made and their spectra measured.

The parent substances of these compounds are, respectively, di-4-pyridylmethane, $(C_5NH_4)_2CH_2$, 2 : 4′-dipyridylmethane, di-2-pyridylmethane, di-2-pyridylamine, $(C_5NH_4)_2NH$, and (for the three kinds of carbocyanine) 4 : 4′-, 2 : 4′-, and 2 : 2′-dipyridylpropenes, $C_5NH_4{\cdot}CH_2{\cdot}CH{:}CH{\cdot}C_5NH_4$. Miss Hamer was kind enough to present me with a specimen of di-2-quinolylamine, and I have succeeded in making the third substance and its methyl derivatives. Observations of these were sufficient, taken along with published data, to solve the problem.

Scheibe and Rossner (*Ber.*, 1921, **54**, 786) made the very significant discovery that di-2-quinolylmethane, which is a nearly colourless substance, can be converted by dilute acid, at about $p_H = 5$, into a coloured phase which has practically the same absorption spectrum as *ψ-iso*cyanine (which is the dimethyl derivative of this diquinolylmethane). The colour of the *ψ-iso*cyanine salts is therefore due to the stable activation of the molecule by the methyl groups, which render the nitrogen atom (or possibly both nitrogen atoms) permanently quinquevalent.

There is a minute difference between the colours of *ψ-iso*cyanine salts and of activated di-2-quinolylmethane: the observations show that the methyl "colour-factor" has the value 1·005 (λ 521 for the former, and λ 516 * for the latter—referring to the highest band of each: the square root of the ratio of these figures is the methyl colour-factor).

Similarly, comparison of my observations on activated diquinolylmethane with those on activated dipyridylmethane enables the colour-factor for quinolyl/pyridyl to be calculated; the top band of the latter is at λ 422, whence the colour-factor is $\sqrt{516/422}$, or 1·105.

This figure is much the same as the naphthol/phenol colour-factor previously established in the ordinary dicyclic family of dyes. It shows that the effect of the extra "loading" with a portion of a benzene ring is the same in the two families of colouring matters.

Two other interesting regularities emerge from the observations. (A) All the cyanines have two bands close together, and the ratio of the absorption-centre wave-lengths for the two bands of each substance is practically always 1·065. (B) By a remarkable coincidence also the change of linking from ortho to para [*i.e.*, the change from 2 : 2′ (or *ψ-iso*) to 2 : 4′ (or *iso*), and from *iso* to ordinary (2 : 4′ to 4 : 4′)] involves the same factor 1·065.

These factors therefore cancel in certain cases: the lower band of a 4 : 4′-cyanine is in the same place as the higher band of the

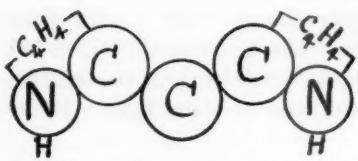
* Author's observations in water: 4 units higher in alcohol.

corresponding 2 : 4′-cyanine, and the lower band of the latter is in the same place as the higher band of the corresponding 2 : 2′-cyanine.

The whole of the family having thus been regularised, it is only necessary to consider a single example, *viz.*, the simplest one, di-2-pyridylmethane, in order to find the distance between the positive centres on which the colour depends.

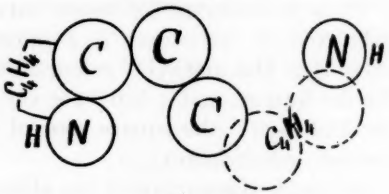
The formula of this substance may be written $C_4H_4NC{\cdot}C{\cdot}CNC_4H_4$ (H_2), in which the atoms in positions 3, 4, 5, and 6 of the pyridine rings are written as C_4H_4. For the molecule in the activated condition, this becomes $C_4H_4(NH)C{:}C{:}C(NH)C_4H_4$. Since the C_4H_4 groups lie obliquely to the chain NCCCN a small allowance may be made for this type of "loading" (see J., 1924, **125**, 1139). The activated substance being found to have λ 422, the value λ 415 may be attributed to the chain NCCCN. From the graph in Part III the distance between the centres of the nitrogen atoms in this chain is found to be 5·33 tenth-metres.

FIG. 1.



Di-2-pyridylmethane.

FIG. 2.



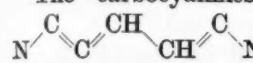
2 : 4′*Dipyridylmethane.*

Now if the five atoms were in a straight line, the distance would be (using Bragg's data) (3 × 1·54) + (2 × 0·65) or 5·92 tenth-metres. If the five atoms are arranged alternately (zigzag) at 109½°, *viz.*, N–C–C–C–N, the distance between the nitrogen centres is about 4·9 tenth-metres. If they are arranged in the same manner but with the double-bond angle of 125¼° between each carbon atom, *viz.*, N–C=C–C–N, the distance is at 5·26 tenth-metres; which is sufficiently near what is required. Fig. 1 represents the result drawn to scale. It is to be noted that the central carbon atom is almost in line with the two nitrogen atoms. The diagram for dimethyl-*ψ-iso*cyanine iodide would be the same, with C_8H_6 for C_4H_4, two methyl groups on the nitrogen atoms, and HI added. The diagram for dimethyl*iso*cyanine iodide would be as the foregoing, but with one nitrogen para to the central carbon atom, as shown for its parent-substance, 2 : 4′-dipyridylmethane, in Fig. 2. Since the shape of the pyridine ring is not yet known, Fig. 2 cannot

be drawn to scale. Similarly, if both nitrogen atoms are para to the central carbon atom, the distance between the nitrogen centres is still farther increased, and the diagram for ordinary cyanine (which is blue, with λ 590, when examined in water) is obtained.

In the opinion of the author the subsidiary band of the cyanines is to be accounted for by a small alteration in one of the angles of the (otherwise rigid) configuration shown, say from 125° to 109°.

The azocyanine family appears to be abnormal in one respect, inasmuch as the unmethylated member does not become activated with acid. In consequence the effect of the methyl groups is large (factor 1·06 instead of 1·005; see p. 2339).

The carbocyanines probably have the zigzag arrangement  , in which all the angles are 125¼°, except one, which is smaller. On account of the great "loading" the distance between the nitrogen centres need not be greater than 6 or 6½ tenth-metres to agree with the high colour of these substances. The other factors have the same effect in this series as in the cyanine series (kryptocyanine λ 711, 2 : 4′-carbocyanine λ 657, pinacyanole λ 607).

The author's restrictive definition of the term "auxochrome" must be expanded to meet these cases, for it is obvious that nitrogen in a ring is the auxochrome of the cyanine family quite independently of its being alkylated or not: similarly, oxygen in a ring is the auxochrome of the natural phenylbenzopyranole colours and also of fluorescein in its acid phase. The terms auxochrome and hapton really connoted an intermediate stage in the rejection of the German theory of colour, and are now themselves generalised and replaced by the conception of two positive centres; a conception which, combined with that of comparative molecular rigidity, is probably capable of explaining all colour phenomena (Part III, *loc. cit.*).

Experimental.

The syntheses were all performed by adding phosphorus pentachloride to a warm mixture of quinaldine (or methylquinaldinium iodide, or picoline, or methylpicolinium iodide, according to the substance required) and 2-pyridone (or carbostyril). The latter two substances were made from pyridine or quinoline by means of hypochlorous acid (Einhorn and Lauch, *Annalen*, 1888, **243**, 343). The yield is poor; but the materials are cheap.

Di-2-pyridylmethane, from picoline and 2-pyridone, is deep yellow in water containing a little alcohol and acetic acid: λλ about 422 and 399. In the unactivated condition it is pale, and the upper band is absent.

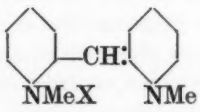
1-Methyldi-2-pyridylmethane, from methylpicolinium iodide and 2-pyridone, appears to be yellow (activated) under all conditions: λλ about 425 and 400.

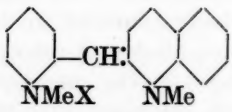
2-Pyridyl-2-quinolylmethane, from quinaldine and pyridone or from picoline and carbostyril, is orange when activated and yellow when neutral. The bands are vague, but are roughly at λλ 460 and 434. There are two possible *N*-methyl derivatives of this substance, *viz.*, quinolyl-methylpyridyl-methane, $C_9H_6N{\cdot}CH{:}C_5H_4NMe$ or $C_9H_7N{:}C{:}C_5H_4NMe$, and pyridyl-methylquinolyl-methane, $C_5H_4N{\cdot}CH{:}C_9H_6NMe$ or $C_5H_5N{:}C{:}C_9H_6NMe$. Both are orange-brown in dilute acetic acid, but the preparations were unsatisfactory; both have much the same absorption, in which the upper band is abnormally faint: observed λλ 488 and 460.

Di-2-quinolylmethane, from quinaldine and carbostyril, is, as Scheibe states, pale in colour, but can be activated by dilute acetic acid so as to exhibit the high colour of dimethyl-ψ-*iso*cyanine salts. The lower band is at about λ 490 (see p. 2339 for the comparison with the cyanine).

The 1-methyl derivative of the foregoing has a colour and a spectrum almost identical with those of dimethyl-ψ-*iso*cyanine iodide: observed λλ 519 and 490.

Small quantities of the unknown primitive cyanines have been prepared. 1 : 1′-Dimethyldi-2-pyridylmethane hydroxide anhydride (I) (which the author suggests should be named dimethylprotocyanine) is yellow in solution with λλ 428 and 405. It is the

(I.) 



(II.)

pyridine analogue of dimethyl-ψ-*iso*cyanine. The intermediate substance (II) is orange in solution and has apparently three bands, at λλ 495, 465, and 430, the lowest being the strongest. The author suggests the name dimethylmesocyanine for this substance.

Observations in water of Miss Hamer's nitrogen-analogues of the 2 : 2′-cyanines (J., 1924, **125**, 1348) gave the following results:

Dimethylazocyanine: λλ 421 and 396 (this is 4 units lower than the discoverer's observation in alcohol).

Methyldiquinolylamine (termed by Miss Hamer methyldihydroquinolenylquinolylimine): λλ 420 and 394.

Di-2-quinolylamine in acetic acid: λλ 371 and 350.

2-Aminoquinoline in acetic acid: λ 340 broad (similar to carbostyril: λ 327).

Both diquinolylamine and dimethylazocyanine have the same

absorption in concentrated sulphuric acid solution, *viz.*, narrow bands at λλ 375 and 358.

Summary.

1. The positions of the bands of the cyanines are calculated by multiplying those of the *iso*cyanines by 1·065.
2. Those of the *iso*cyanines are obtained from those of the ψ-*iso*cyanines by means of the same factor.
3. Those of the ψ-*iso*cyanines are practically the same as those of di-2-quinolylmethane activated by very weak acid.
4. Those of diquinolylmethane are derived from those of dipyridylmethane by multiplying by the square of the factor 1·105.
5. The bands of activated dipyridylmethane are explained on the author's spatial theory of colour.
6. The factor 1·065 (for calculating the positions of the bands of 4 : 4′-compounds from those of 2 : 4′-compounds or 2 : 4′-compounds from those of 2 : 2′-compounds) holds good also in the carbocyanine series.

GOVERNMENT LABORATORY, JOHANNESBURG. [*Received, May 11th,* 1925.]

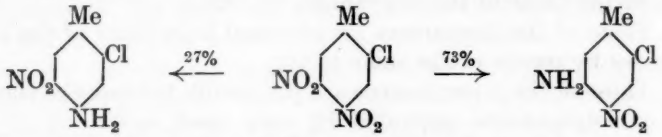
CCCXIX.—*The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus. Part VIII.* 2 : 3- *and* 2 : 5-*Dinitro*-p-*chlorotoluenes.*

By JAMES KENNER, CHARLES WILLIAM TOD, and ERNEST WITHAM.

IT is well recognised that, in spite of much careful work, pre-eminently by Holleman, our present knowledge of the processes of substitution of the benzene nucleus does not permit complete confidence in forecasting the behaviour of more complicated derivatives towards substituting agents. The discussions in previous papers of this series indicate that this difficulty is perhaps less marked in the case of the mobility of substituents in aromatic nitro-derivatives; some instances of exceptional behaviour, however, are on record (compare, *e. g.*, Robinson and Robinson, J., 1917, **111**, 944).

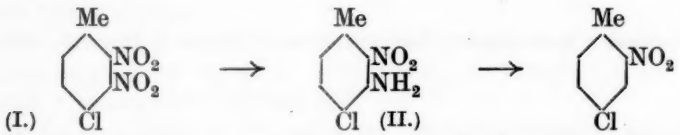
The difference between the two cases possibly lies in the fact that in ordinary substitution we do not yet know how to determine from which point, if any, in the nucleus to calculate the directive effect, whereas it seems clear that the mobility referred to is primarily determined by nitro-groups and that ortho-para-directive substituents produce subsidiary effects only. In certain cases, however, these are decisive, and it is therefore of importance to compare

the effects produced by different substituents. For example, Morgan and his collaborators (J., 1920, **117**, 784; 1921, **119**, 1537) showed that 2-chloro-4 : 5-dinitrotoluene, on treatment with alcoholic ammonia, is converted into a mixture of the two possible chloronitrotoluidines, in which the *m*-derivative predominates:



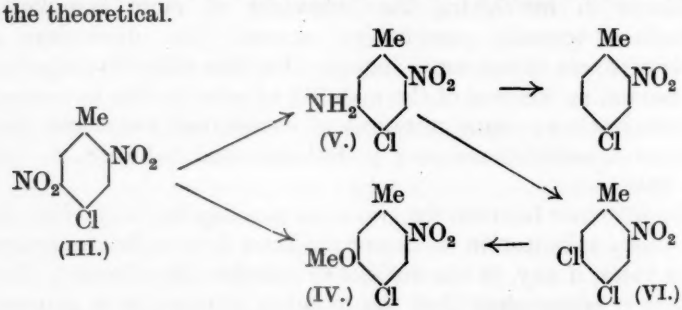
We have now supplemented this result by experiments on 4-chloro-2 : 3-dinitrotoluene (I) and the corresponding 2 : 5-derivative (III).

4-*Chloro*-2 : 3-*dinitrotoluene*, prepared from 2 : 3-dinitro-*p*-toluidine (Scott and Robinson, J., 1922, **121**, 844), was converted by methyl-alcoholic ammonia at 150° into 4-*chloro*-2-*nitro*-m-*toluidine* (II), which was isolated to the extent of 70% of that theoretically possible:



As indicated, the constitution of the product was established by its conversion into the known 4-chloro-2-nitrotoluene. No 4-chloro-3-nitro-*o*-toluidine was isolated in these experiments.

4-*Chloro*-2 : 5-*dinitrotoluene* was similarly converted into a mixture of products, from which, by a somewhat lengthy process of separation, 4-*chloro*-6-*nitro*-m-*tolyl methyl ether* (IV), accompanied by a small quantity of the *m*-cresol itself, and 4-*chloro*-6-*nitro*-m-*toluidine* (V) were obtained, the yields being respectively 20 and 30% of the theoretical.



By elimination of the amino-group, the base (V) furnished 4-chloro-2-nitrotoluene, whilst in order to establish the constitution of the methyl ether (IV), the base was converted into a 4 : 5-*dichloro*-

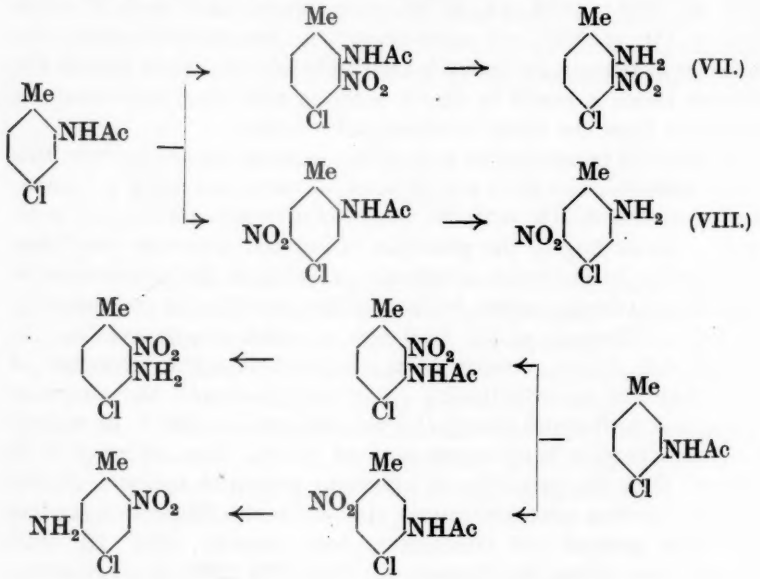
2-*nitrotoluene* (VI), from which a product identical with the ether was easily prepared by treatment with sodium methoxide. No other definite products could be isolated from the above mixture, and it appeared that the tarry residues consisted of azo- or azoxy-derivatives.

In each of the three chlorodinitrotoluenes, therefore, the group that is displaced is the one in the meta-position to the methyl group rather than that in the meta-position to the chlorine atom, and it cannot be doubted that some fundamental difference between these substituents is here involved. If we accept the evidence, derived from the behaviour of 3 : 4-dinitrotoluene (Kenner and Parkin, J., 1920, **117**, 852) and 3 : 4-dinitrochlorobenzene (Laubenheimer, *Ber.*, 1876, **9**, 1826; 1878, **11**, 1156), respectively, that each of them favours the mobility of nitro-groups in the meta-position, the influence of the methyl group is seen to be stronger than that of the chlorine atom, a result in direct contrast with that arrived at by Holleman from the study of direct substitution.

It would be premature to deduce any general conclusion from this single instance, but it is not at once obvious how such a contradiction is reconcilable with the theory of alternate strong and weak bonds. According to the principle of induced alternate polarities, on the other hand, direct substitution consists in the replacement of a positive hydrogen atom, whilst mobile substituents are negative, so that a difference of the kind now revealed is conceivable. As against this, it has recently been suggested that the behaviour of nitrosobenzene on substitution "distinctly favours" the alternate strong and weak bond theory (Ingold, this vol., p. 515). In reality, however, there is here a confusion of issues. For, although it is claimed that the principle of alternate polarities operates in the benzene nucleus and determines the point of substitution, it has also been pointed out (Robinson, *Ann. Reports*, 1922, **19**, 102; compare also Allsop and Kenner, J., 1923, **123**, 2296) that erroneous conclusions may arise from writing positive and negative signs in any group whatsoever. In such circumstances, the only proper procedure in investigating the validity of the polarity principle consists in determining, from its directive effect, which sign must, according to the principle, be assigned to a given group, and then ascertaining whether this conclusion accords with the general behaviour of the group in other directions. Thus Ingold's result would indicate that the nitroso-group is negative and hence should be comparable with chlorine and hydroxyl, so that the typical behaviour of these, when "positive" properties are imposed on them, as in hypochlorous acid and hydrogen peroxide, should be reproduced by nitrous acid. This is well known to be the case in

the reaction with hydrogen iodide, so that Ingold's result cannot be accepted as evidence against the polarity principle. It remains, of course, to be explained why the nitroso-group as a whole reacts as though endowed with negative properties, and it seems questionable whether valid evidence on this point can be deduced from reactions, *e.g.*, those with the Grignard reagent and with ethyl malonate, in which the group is broken up.

In order to place the above results on a still surer foundation, the bases already mentioned, together with those alternatively possible, namely 4-*chloro*-3-*nitro*-o-*toluidine* (VII) and 4-*chloro*-5-*nitro*-o-*toluidine* (VIII), were synthesised by the aid of reactions briefly represented in the following scheme:



EXPERIMENTAL.

Nitration of 4-*Chloroaceto*-o-*toluidide*.—A mixture of the finely-powdered compound (20 g.) with glacial acetic acid (30 c.c.) and sulphuric acid (40 c.c.) was thoroughly stirred and maintained at 10—15° during the addition of fuming nitric acid (*d* 1·5; 6 c.c.). After diluting the resulting stiff paste with ice-water, the solid material was collected, dried, and hydrolysed by boiling with 50% sulphuric acid (400 c.c.). From the mixture of weak bases precipitated by dilution with water, 4-*chloro*-5-*nitro*-o-*toluidine*, m. p. 163—164° (Found: N, 15·4. $C_7H_7O_2N_2Cl$ requires N, 15·0%), was isolated by crystallisation from benzene. Its *acetyl* derivative,

prepared by using a mixture of acetic anhydride and acetyl chloride, separated from benzene in prisms, m. p. 181—182° (Found : N, 12·3. $C_9H_9O_3N_2Cl$ requires N, 12·3%). 5-*Chloro*-2-*methyl*-p-*phenylenediamine*, obtained from the nitro-base by reduction in glacial acetic acid solution with stannous chloride and hydrochloric acid, crystallised from benzene–light petroleum in white leaflets, m. p. 145—146° (Found : N, 17·9. $C_7H_9N_2Cl$ requires N, 18·1%). The compound, m. p. 146°, of unknown orientation prepared by Vorländer (*Ber.*, 1901, **34**, 1652) from *N*-nitroso-*o*-tolylglycine was doubtless the same. The base responded to Lauth's test, and its acetyl derivative melted at 301°. The hydrochloride was prepared by Vehrmann (*Ber.*, 1915, **48**, 2028) from 4-chloro-2 : 5-dinitrotoluene.

4-*Chloro*-3-*nitro*-o-*toluidine*, light brown needles, m. p. 60—62·5°, was contained in the mother-liquors from the crystallisation of the 5-nitro-isomeride, and isolated by distillation in steam and repeated crystallisation from benzene–light petroleum (Found : N, 15·2. $C_7H_7O_2N_2Cl$ requires N, 15·0%). The *acetyl* derivative, m. p. 194—195°, prepared by means of acetic anhydride in presence of sulphuric acid, separated from benzene in small prisms (Found : N, 12·5. $C_9H_9O_3N_2Cl$ requires N, 12·3%).

Nitration of 4-*Chloroaceto*-m-*toluidide*.—This compound, previously described by Goldschmidt and Hönig (*Ber.*, 1886, **19**, 2411) as melting at 97°, was obtained in white needles, m. p. 102°. The nitration of the material, and hydrolysis of the product were performed as described in the case of the o-isomeride. Finally, steam was passed directly into the acid hydrolysis mixture until the melting point of the solid distillate was above 50°.

4-*Chloro*-6-*nitro*-m-*toluidine* was obtained after diluting the liquor in the distillation flask with hot water and filtering from tarry matter; it crystallised from dilute alcohol in yellow needles (15 g.), m. p. 120—121° (Found : N, 15·2. $C_7H_7O_2N_2Cl$ requires N, 15·0%). It was converted by reduction into 5-chloro-2-methyl-*p*-phenylenediamine, and its *acetyl* derivative, prepared by means of acetic anhydride and sulphuric acid, separated from dilute alcohol in white leaflets, m. p. 134—135° (Found : N, 12·3. $C_9H_9O_3N_2Cl$ requires N, 12·3%).

4-*Chloro*-2-*nitro*-m-*toluidine* was the chief constituent of the above solid steam-distillate. It was redistilled from 50% sulphuric acid solution with steam and then crystallised from dilute alcohol, lemon-yellow needles (4 g.), m. p. 52—53°, being thus obtained (Found : N, 15·1. $C_7H_7O_2N_2Cl$ requires N, 15·0%). The orientation of the base follows from its identity with the base obtained from 4-chloro-2 : 3-dinitrotoluene (*v. infra*). Its *acetyl* derivative, m. p. 210—212°, prepared by means of acetic anhydride, separated from

absolute alcohol in small prisms (Found: N, 12·7. $C_9H_9O_3N_2Cl$ requires N, 12·3%).

4-Chloro-6-nitro-m-tolyl Methyl Ether.—4-Chloro-6-nitro-*m*-toluidine (5 g.) was diazotised by Gattermann's method (*Annalen*, 1912, **393**, 200) by solution in nitrosylsulphuric acid (33 g. equiv. to 1·8 g. of sodium nitrite). The solid produced on adding the cooled solution to a solution of cuprous chloride (2 g.) in hydrochloric acid (18 g.) at 0° was collected and distilled in steam. 4 : 5-Dichloro-2-nitrotoluene (3 g.), thus obtained, separated from methyl alcohol in yellow needles, m. p. 63° (compare Cohen and Dakin, J., 1902, **81**, 1349). When the dichloro-compound (3 g.) was heated at 100° with a solution of sodium (0·3 g.) in methyl alcohol (12 c.c.) for 7 hours, the solution became neutral and contained *4-chloro-6-nitro-m-tolyl methyl ether* (2·33 g.), which separated from methyl alcohol in light straw-coloured needles, m. p. 121—122° (Found: N, 7·1. $C_8H_8O_3NCl$ requires N, 6·9%).

4-Chloro-2 : 3-dinitrotoluene.—This compound, prepared from 2 : 3-dinitro-*p*-toluidine (Scott and Robinson, *loc. cit.*; Page and Heasman, J., 1923, **123**, 3235) by the process described in the case of 4 : 5-dichloro-2-nitrotoluene, crystallised from benzene–light petroleum in long, lemon-yellow prisms, m. p. 106·5° (Found: N, 13·1. $C_7H_5O_4N_2Cl$ requires N, 12·9%).

Action of Methyl-alcoholic Ammonia on 4-Chloro-2 : 3-dinitrotoluene.—The chloro-compound (4·32 g.) was heated with methyl alcohol (54 c.c.) and ammonia (*d* 0·880; 10 c.c.) for 8 hours at 140—150°. After removing alcohol from the product and distilling the residue in steam, a solid material (3·8 g.) was obtained in a practically pure condition. It separated from dilute alcohol in light yellow needles, m. p. 52—53°, and was identified as 4-chloro-2-nitro-*m*-toluidine (*a*) by comparison with an authentic specimen and (*b*) by degradation to 4-chloro-2-nitrotoluene by adding a diazotised solution of the base (1 g.) in nitrosylsulphuric acid (6·6 g.) to boiling absolute alcohol (200 c.c.) and distilling the product in steam after removal of the alcohol.

Action of Methyl-alcoholic Ammonia on 4-Chloro-2 : 5-dinitrotoluene.—The chloro-compound, prepared by Kehrmann's method (*Annalen*, 1898, **303**, 1; *Ber.*, 1915, **48**, 2028), was heated with the same proportions of methyl alcohol and ammonia as the 2 : 3-isomeride, but for 16 hours at 160°. The product left after removing the alcohol was extracted with six successive quantities of boiling concentrated hydrochloric acid (50 c.c.). The residue (0·86 g., m. p. 100—104°), after treatment with benzene to remove tarry material, furnished almost pure 4-chloro-6-nitro-*m*-tolyl methyl ether (0·63 g.), which did not depress the melting point of an authentic specimen.

A further quantity (0·95 g.) of the same compound was isolated in a similar manner from the material (1·75 g.) deposited by the acid extracts on cooling. In addition, these yielded a product (0·1 g., m. p. 130—135°), which was soluble in alkali and converted by treatment with methyl sulphate into the same ether. Evidently the product was 4-chloro-6-nitro-*m*-cresol. On diluting the cold acid extract with water, a precipitate (3·34 g.) was obtained, from which 4-chloro-6-nitro-*m*-toluidine (1·92 g., m. p. 120—121°) was isolated by extraction with benzene and crystallisation from alcohol. The base was identified by comparison with an authentic specimen, and by conversion into 4-chloro-2-nitrotoluene. A further quantity (0·3 g.) of the same amine was isolated from the crude base (0·49 g.) precipitated when the residual diluted acid liquor was rendered alkaline with ammonia. No pure material was furnished by the sticky substance (0·3 g.) obtained by extracting the alkaline filtrate with ether. In all the above cases, the end fractions were treated with acetic anhydride and acetyl chloride, but no definite acetyl derivatives were obtained, and it was assumed that the materials were azo- or azoxy-derivatives.

Action of Sodium Methoxide on 4-Chloro-2 : 5-dinitrotoluene.—When this compound (5 g.) had been heated for 2 hours at 100° with a solution of sodium (0·5 g.) in methyl alcohol (20 c.c.), the liquid was neutral and yielded 4-chloro-6-nitro-*m*-tolyl methyl ether (5·7 g.).

One of us (C. W. T.) expresses grateful acknowledgment of a grant from the Department of Scientific and Industrial Research which enabled him to participate in this work. Further, we wish to thank the Research Fund Committee of the Chemical Society for a grant towards the expenses of this investigation.

THE UNIVERSITY, SHEFFIELD. [*Received, August 10th*, 1925.]

CCCXX.—*The Formation of Chromones.—A Criticism.*

By WILSON BAKER.

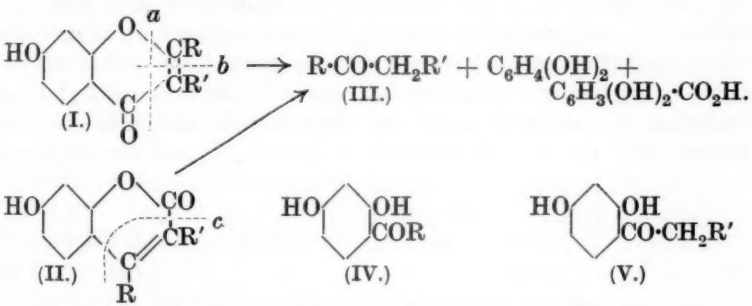
IN a recent paper by Baker and Robinson (this vol., p. 1981) the view was put forward that the products described in a series of four papers on the synthesis of γ-benzopyrones or chromones (Jacobson and Ghosh, Parts I, II, and III, J., 1915, **107**, 424, 959, 1051; Ghosh, J., 1916, **109**, 106) are, in reality, the isomeric α-pyrones or coumarins, the substituent in position 2 of the chromones occupying position 4 in the coumarins. Since this criticism concerned twenty-four fundamental compounds and about

sixty derivatives thereof, it was considered desirable to investigate the subject further. A more detailed study has confirmed the view that all the products described in those papers are coumarins. no fewer than thirteen of the true chromones having now been prepared.

In the experiments described in the first three papers, substituted acetoacetic esters, $CH_3{\cdot}CO{\cdot}CHR{\cdot}CO_2Et$ (where R = benzyl, phenyl, or benzoyl), ethyl α-benzoyl-β-phenylpropionate, and ethyl α-phenylformylacetate were condensed with phenols usually in presence of concentrated sulphuric acid, but acetic acid and zinc chloride, or acetic acid and hydrogen chloride, were also used. In the cases of benzoylacetoacetic ester and ethyl acetylmalonate coumarins were admittedly produced. It is now clear that under such conditions coumarins are always formed, though it must be noted that with other condensing agents chromones may be produced. For example, Simonis and his collaborators have prepared chromone derivatives by condensing acetoacetic ester, and its methyl and ethyl derivatives, with phenols in presence of phosphoric anhydride (Petschek and Simonis, *Ber.*, 1913, **46**, 2015; Simonis and Lehmann, *Ber.*, 1914, **47**, 697; Simonis and Remmert, *ibid.*, p. 2229; see also Heilbron, Barnes, and Morton, J., 1923, **123**, 2569), the reaction being apparently of a general character.

In the fourth paper, nitriles of the type $R{\cdot}CHPh{\cdot}CN$ (where R = acetyl, formyl, or benzoyl) and benzoylacetonitrile were condensed with phenols usually in presence of sulphuric acid, but other condensing agents employed were acetic acid and hydrogen chloride, and phosphoryl chloride. The substances prepared from the nitriles corresponding to the carboxylic esters employed in the preceding papers were identical with the products prepared from those esters. Examination of the literature showed that it was exceedingly improbable that these condensations would produce chromones. For example, Meyer (*J. pr. Chem.*, 1903, **67**, 342) condensed benzoacetodinitrile, $NH{:}CPh{\cdot}CH_2{\cdot}CN$, with resorcinol in presence of concentrated sulphuric acid and obtained a product which was considered to be 7-hydroxyflavone, but which has subsequently been proved by Sonn (*Ber.*, 1918, **51**, 821) to be the isomeric 7-hydroxy-4-phenylcoumarin. Again, Bargellini and Forti-Forli (*Gazzetta*, 1911, **41**, i, 747) showed that by condensing *p*-methoxybenzoylacetonitrile and resorcinol by means of sulphuric acid, 7-hydroxy-4-*p*-methoxyphenylcoumarin is produced, and from the same nitrile Sonn (*loc. cit.*) has prepared 5 : 7-dihydroxy-4-*p*-methoxyphenylcoumarin (see also Sonn, *ibid.*, p. 1829). The present work has now fully established the fact that all such condensations of nitriles with phenols produce coumarins.

The constitutions of Ghosh's products were taken to be established by the fact that on hydrolysis with 33% or 50% aqueous potassium hydroxide they gave a neutral ketone, an *o*-hydroxy-acid, and in four cases (wherever it was sought) resorcinol; but in all, only five resorcinol derivatives were submitted to hydrolysis and these have all been definitely shown to be coumarins. The only other compounds submitted to hydrolysis were two derived from α-naphthol and one from *m*-cresol. The scheme given was as shown below, the supposed chromone (I) (really the isomeric coumarin II) undergoing hydrolysis along the dotted line *a*, giving the ketone (III), β-resorcylic acid, and resorcinol; whilst it was stated (Part I, *loc. cit.*, p. 427) that the complete hydrolysis of the coumarin (II) would produce the hydroxy-ketone (IV) and the acid $R'\cdot CH_2\cdot CO_2H$. But there seems very little experimental evidence to support such a method of fission, and it is shown below that the hydrolysis of coumarins, if it proceeds further than the mere opening of the pyrone ring, almost invariably takes quite another course. It is significant that in no case was a hydroxy-ketone of the type V produced, which is usually found as one of the products of alkaline decomposition of true chromones, owing to hydrolysis along the dotted line *b*.



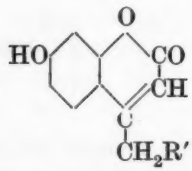
It follows that the production of the same neutral ketone is possible both from the chromone (I) and from the isomeric coumarin (II), owing, in the latter case, to hydrolysis along the line *c*. This is borne out by the fact that Jacobson and Ghosh's so-called 7-hydroxy-3-benzyl-2-methylbenzo-γ-pyrone (Part I, *loc. cit.*) (really 7-hydroxy-3-benzyl-4-methylbenzo-α-pyrone) gave on hydrolysis benzylacetone and β-resorcylic acid, whilst the true chromone (Crabtree and Robinson, J., 1918, **113**, 859) gave benzylacetone and benzylresacetophenone. It is seen, moreover, that the hydrolysis of (IV) along the line *c* accounts for the production of resorcinol, the formation of which is unsatisfactorily explained by Jacobson and Ghosh (J., 1915, **107**, 960) by assuming the decomposition of

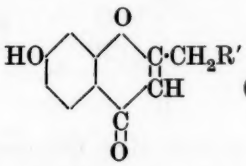
β-resorcylic acid in presence of alkali. The method of production of β-resorcylic acid is not so obvious.

This course of hydrolysis of a coumarin appeared so novel that it was considered desirable to establish it beyond doubt. For this purpose the preparation and hydrolysis of Ghosh's so-called 7-hydroxy-3-phenyl-2-methylbenzo-γ-pyrone (which has since been proved to be 7-hydroxy-3-phenyl-4-methylbenzo-α-pyrone, Baker and Robinson, *loc. cit.*) were repeated, and the formation of benzyl methyl ketone (characterised by means of its semicarbazone and phenylhydrazone), resorcinol, and β-resorcylic acid was confirmed. From 3 g. of this coumarin were obtained about 0·5 g. of benzyl methyl ketone, a slightly smaller quantity of resorcinol, and only a very small amount of β-resorcylic acid, whilst some of the material was unhydrolysed. This confirms the view given above that the principal reaction is the production of benzyl methyl ketone and resorcinol, the β-resorcylic acid being only a by-product, and differs from Ghosh's view, that the chief reaction is the production of benzyl methyl ketone and β-resorcylic acid, the resorcinol being the by-product.

The important conclusion follows from these observations that the only safe criterion of the production of a chromone (I) and not the coumarin (II), is the formation on hydrolysis of a hydroxyketone (V), and shows the necessity for extreme caution in deciding the constitution of such substances by hydrolysis. The matter, however, is further complicated in cases where R = methyl (thus including the present), since not only can (I) and (II) give the ketone (III), but also the isomeric coumarin (VI) and the chromone

(VI.)





(VII.)

(VII). As proof of this, the compounds (I) and (VI), having R′ = phenyl (Baker and Robinson, *loc. cit.*), were submitted to hydrolysis under the conditions employed by Ghosh in the case of (II), the main results of which were verified as described above. Compound I underwent complete hydrolysis and gave a small amount of benzyl methyl ketone and about a 70% yield of 2 : 4-dihydroxyphenyl benzyl ketone; whilst compound VI, though incompletely hydrolysed, gave a relatively large yield of benzyl methyl ketone and resorcinol. The benzyl methyl ketone was in all cases characterised by means of its semicarbazone and phenylhydrazone, and the

melting points of mixtures of any of the specimens showed no depression. Compound VII (Hannach and Kostanecki, *Ber.*, 1902, **35**, 866) has not actually been hydrolysed under these conditions, but there is no doubt that it also would give benzyl methyl ketone as one of its fission products.

In the following paragraphs are given the correct properties of the compounds named and those of their derivatives, the first substance of each pair having previously been wrongly described by Jacobson and Ghosh and by Ghosh as the second. A comparison of the fluorescences of the two classes of compounds is not made, since both chromones and coumarins frequently show almost identical fluorescences under similar conditions.

The chromones described in this paper were prepared by the well-known reaction from ketones of the type V (where R′ = phenyl or benzyl) by acylation with a mixture of the anhydride and sodium salt of acetic or benzoic acid. Three of the necessary ketones (two previously unknown) were prepared by an application of the Hoesch synthesis.

Part I (*loc. cit.*): 7-Hydroxy-3-benzyl-4-methylbenzo-α-pyrone, m. p. 186°; acetyl derivative, m. p. 168°; methyl ether, m. p. 119°. 7-Hydroxy-3-benzyl-2-methylbenzo-γ-pyrone, m. p. 282°; acetyl derivative, m. p. 121°; methyl ether, m. p. 109° (Crabtree and Robinson, J., 1918, **113**, 867).

3-Benzyl-4 : 7-dimethylbenzo-α-pyrone, m. p. 117°. This preparation was originally carried out by Fries and Klostermann (*Annalen*, 1908, **362**, 27), and the correct constitution assigned to the compound.

7 : 8-Dihydroxy-3-benzyl-4-methylbenzo-α-pyrone, m. p. 185°; diacetyl derivative, m. p. 172°. 7 : 8-Dihydroxy-3-benzyl-2-methylbenzo-γ-pyrone, m. p. 203—205°; diacetyl derivative, m. p. 126° (this paper).

7-Hydroxy-3-benzyl-4 : 5-dimethylbenzo-α-pyrone, m. p. 177—178°; acetyl derivative, m. p. 169°. 7-Hydroxy-3-benzyl-2 : 5-dimethylbenzo-γ-pyrone, m. p. 294—295°; acetyl derivative, m. p. 138—139° (this paper).

5 : 7-Dihydroxy-3-benzyl-4-methylbenzo-α-pyrone, m. p. 218—219°; diacetyl derivative, m. p. 154°. 5 : 7-Dihydroxy-3-benzyl-2-methylbenzo-γ-pyrone, m. p. 200—201°; diacetyl derivative, m. p. 112° (this paper).

Part II (*loc. cit.*): 7-Hydroxy-3-benzyl-4-phenylbenzo-α-pyrone, m. p. 186°; acetyl derivative, m. p. 134°. 7-Hydroxy-3-benzyl-2-phenylbenzo-γ-pyrone, m. p. 272—274°; acetyl derivative, m. p. 150° (this paper).

7 : 8-Dihydroxy-3-benzyl-4-phenylbenzo-α-pyrone, m. p. 136—

137°; diacetyl derivative, m. p. 175°. 7 : 8-Dihydroxy-3-benzyl-2-phenylbenzo-γ-pyrone, m. p. 275—276°; diacetyl derivative, m. p. 175—176° (this paper).

5 : 7-Dihydroxy-3-benzyl-4-phenylbenzo-α-pyrone, m. p. 119°; diacetyl derivative, m. p. 56°. 5 : 7-Dihydroxy-3-benzyl-2-phenylbenzo-γ-pyrone, m. p. 202—203°; diacetyl derivative, m. p. 126° (this paper).

Part III (*loc. cit.*): 7-Hydroxy-3-phenyl-4-methylbenzo-α-pyrone, m. p. 226°; acetyl derivative, m. p. 185°; methyl ether, m. p. 87°. 7-Hydroxy-3-phenyl-2-methylbenzo-γ-pyrone, m. p. 240°; acetyl derivative, m. p. 162°; methyl ether, m. p. 135·5° (Baker and Robinson, *loc. cit.*).

7 : 8-Dihydroxy-3-phenyl-4-methylbenzo-α-pyrone, m. p. 268°; diacetyl derivative, m. p. 211°. 7 : 8-Dihydroxy-3-phenyl-2-methylbenzo-γ-pyrone, m. p. 219—220°; diacetyl derivative, m. p. 115° (this paper).

5 : 7-Dihydroxy-3-phenyl-4-methylbenzo-α-pyrone, m. p. 178°; diacetyl derivative, m. p. 146°. 5 : 7-Dihydroxy-3-phenyl-2-methylbenzo-γ-pyrone, m. p. 228°; diacetyl derivative, m. p. 169° (Baker and Robinson, *loc. cit.*).

Ghosh (*loc. cit.*): 7-Hydroxy-3-phenyl-4-methylbenzo-α-pyrone, identical with the product prepared in Part III.

7 : 8-Dihydroxy-3-phenyl-4-methylbenzo-α-pyrone, identical with the product prepared in Part III.

7-Hydroxy-3 : 4-diphenylbenzo-α-pyrone, m. p. 288°; acetyl derivative, m. p. 222°, and which on hydrolysis with 33% aqueous potassium hydroxide for 4 hours gave deoxybenzoin, resorcinol, and β-resorcylic acid. 7-Hydroxy-2 : 3-diphenylbenzo-γ-pyrone, m. p. 270—271°; acetyl derivative, m. p. 208—209° (Baker and Robinson, *loc. cit.*), and has now been found to give on hydrolysis under the above conditions a 93% yield of 2 : 4-dihydroxyphenyl benzyl ketone and benzoic acid.

7 : 8-Dihydroxy-3 : 4-diphenylbenzo-α-pyrone, m. p. 185°. 7 : 8-Dihydroxy-2 : 3-diphenylbenzo-γ-pyrone, m. p. 297° (this paper).

7-Hydroxy-4-phenylbenzo-α-pyrone, m. p. 243°. Ghosh's preparation has been repeated and a substance, m. p. 244°, obtained which crystallises, not in needles as stated, but in regular, four-sided plates having all the properties ascribed by Pechmann and Duisberg (*Ber.*, 1883, **16**, 2126) and Pechmann and Hancke (*Ber.*, 1901, **34**, 356) to 7-hydroxy-4-phenylbenzo-α-pyrone. Further, the melting point of a mixture with an authentic specimen of 7-hydroxy-2-phenylbenzo-γ-pyrone, m. p. 240°, kindly supplied by Mr. J. Allan (Allan and Robinson, J., 1924, **125**, 2192), showed a depression of about 30°.

Experimental.

Benzylresacetophenone.—A solution of β-phenylpropionitrile (10 g.) (Baker and Lapworth, J., 1924, **125**, 1334) and resorcinol (10 g.) in dry ether (75 c.c.) was saturated with dry hydrogen chloride at 0°. After 48 hours, water was added, the ether distilled off, and the ketimine hydrolysed by heating on the steam-bath for ½ hour. The oily product was extracted with chloroform, the solution shaken with aqueous sodium hydroxide, and the ketone liberated by acid. By recrystallisation from dilute acetic acid it was obtained in colourless needles, m. p. 88° (see Bargellini and Marantonio, *Gazzetta*, 1908, **38**, ii, 514).

7-*Hydroxy*-3-*benzyl*-2-*phenylbenzo*-γ-*pyrone.*—Benzylresacetophenone (5 g.), benzoic anhydride (20 g.), and anhydrous sodium benzoate (5 g.) were heated together at 170—180° for 6 hours. The product was hydrolysed by heating on the water-bath with alcohol (50 c.c.) and 50% aqueous potassium hydroxide (12 g. KOH) for 10 minutes, and the *pyrone* precipitated from the diluted solution by carbon dioxide. By recrystallisation from ethyl alcohol, in which it was sparingly soluble, it was obtained in small, colourless needles, m. p. 272—274° (Found: C, 80·3; H, 4·9. $C_{22}H_{16}O_3$ requires C, 80·5; H, 4·9%). Its colourless solution in aqueous sodium hydroxide shows a slight bluish-green fluorescence. The *benzoyl* derivative separates from alcohol in colourless, silky needles, m. p. 167°. The *acetyl* derivative, prepared by boiling with acetic anhydride for 6 hours and subsequently shaking with water, crystallises from alcohol in colourless prisms, m. p. 150° (Found: C, 77·8; H, 5·1. $C_{24}H_{18}O_4$ requires C, 77·8; H, 4·9%). The colourless solutions of these compounds in concentrated sulphuric acid show a weak blue fluorescence.

Benzylphloracetophenone.—A solution of β-phenylpropionitrile (15 g.) and anhydrous phloroglucinol (14·5 g.) in ether (100 c.c.) was saturated with hydrogen chloride at 0°. Hydrolysis of the ketimine was effected by heating with water on the steam-bath for ½ hour, the oily product dissolved by the addition of sodium hydroxide, the solution extracted with ether to remove non-phenolic substances, and the ketone liberated by a current of carbon dioxide and taken up with ether. Evaporation of the solvent left a pale yellow oil which solidified on stirring. It crystallised from hot water in colourless needles containing $1H_2O$ (Found: H_2O, 6·5. $C_{15}H_{14}O_4,H_2O$ requires H_2O, 6·5%), or in the anhydrous condition from chloroform in small prisms, m. p. 139—140° (Found: C, 69·7; H, 5·5. $C_{15}H_{14}O_4$ requires C, 69·7; H, 5·5%).

5:7-*Dihydroxy*-3-*benzyl*-2-*methylbenzo*-γ-*pyrone.*—A mixture of

anhydrous benzylphloracetophenone (2 g.), anhydrous sodium acetate (2 g.), and acetic anhydride (10 c.c.) was heated at 170—180° for 12 hours. After shaking with water, the *diacetyl* derivative was collected and recrystallised from alcohol, being obtained in colourless needles, m. p. 112° (Found: C, 68·9; H, 4·8. $C_{21}H_{18}O_6$ requires C, 68·8; H, 5·0%). The parent substance obtained by hydrolysis with boiling, dilute sodium carbonate solution and precipitation with acid, crystallised from dilute methyl alcohol in colourless, nacreous plates, m. p. 200—201° (Found: C, 72·1; H, 5·2. $C_{17}H_{14}O_4$ requires C, 72·3; H, 5·0%). Of its colourless solutions in aqueous sodium hydroxide and concentrated sulphuric acid, the latter only shows a weak blue-green fluorescence, which is also exhibited by a solution of the diacetyl derivative in the same solvent.

5 : 7-*Dihydroxy*-3-*benzyl*-2-*phenylbenzo*-γ-*pyrone*.—A mixture of benzylphloracetophenone (2 g.), benzoic anhydride (15 g.), and sodium benzoate (1 g.) was heated at 180—190° for 10 hours. The product was dissolved by heating on the steam-bath with a mixture of alcohol (50 c.c.) and water (5 c.c.), and hydrolysed by continuing to heat for 15 minutes with 50% aqueous potassium hydroxide (10 g. KOH); the product was precipitated from the diluted solution by carbon dioxide. By recrystallisation from methyl alcohol (charcoal) the *pyrone* was obtained in pale yellow prisms, m. p. 202—203°, containing methyl alcohol of crystallisation which is given up before melting (Found: C, 76·5; H, 4·8. $C_{22}H_{16}O_4$ requires C, 76·7; H, 4·7%). Its solution in aqueous sodium hydroxide shows no fluorescence. The *diacetyl* derivative, prepared by the action of acetic anhydride, crystallises from alcohol in pale yellow prisms, m. p. 126° (Found: C, 73·0; H, 4·6. $C_{26}H_{20}O_6$ requires C, 72·9; H, 4·7%). Both substances give pale yellow solutions in concentrated sulphuric acid which show very weak blue-green fluorescences.

Benzylorcacetophenone.—A solution of β-phenylpropionitrile (15 g.) and anhydrous orcinol (15 g.) in ether (100 c.c.) was saturated with hydrogen chloride at 0°. After 48 hours, the yellow crust of the ketimine was washed with ether and hydrolysed by heating on the steam-bath with water for ½ hour. The resulting oily ketone partly crystallised on standing for several days, consisting doubtless of a mixture of benzylorcacetophenone and the isomeric 2 : 6-dihydroxy-4-methylphenyl β-phenylethyl ketone. The product was pressed on porous earthenware, and the residue crystallised from a large volume of boiling water, shining, pearly plates, m. p. 118·5°, being obtained (Found: C, 75·1; H, 6·1. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·3%). This ketone is proved to be benzylorcaceto-

phenone and not the isomeride by the fact that the benzo-γ-pyrone prepared from it has the properties of a 7- and not a 5-hydroxy-compound (see below).

7-*Hydroxy*-3-*benzyl*-2 : 5-*dimethylbenzo*-γ-*pyrone*.—The *acetyl* derivative obtained in the usual manner from benzylorcacetophenone by acetylation for 20 hours crystallised from methyl alcohol in colourless prisms, m. p. 138—139° (Found: C, 74·7; H, 5·7. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6%). The parent substance obtained by its hydrolysis with aqueous sodium carbonate crystallised from alcohol, in which it was sparingly soluble, in colourless needles, m. p. 294—295° (Found: C, 77·2; H, 5·9. $C_{20}H_{18}O_4$ requires C, 77·1; H, 5·8%). It dissolves readily in warm, dilute sodium hydroxide, giving a colourless solution showing a blue fluorescence. By methylation with methyl sulphate and potassium hydroxide at about 50°, it readily gave a *methyl* ether which crystallised from a small quantity of methyl alcohol in long, colourless prisms, m. p. 109°. All these substances give in concentrated sulphuric acid colourless solutions showing a blue fluorescence.

7 : 8-*Dihydroxy*-3-*phenyl*-2-*methylbenzo*-γ-*pyrone*.—Crude 2 : 3 : 4-trihydroxyphenyl benzyl ketone (10 g.; Noelting and Kadiera, *Ber.*, 1906, **39**, 2057) was acetylated in the usual manner for 24 hours. The oil obtained on treatment with water was extracted with ether, the extracts were shaken with aqueous sodium hydroxide to remove a small quantity of a phenolic substance, dried, and the ether was distilled, leaving a pale brown oil which rapidly crystallised. This *diacetyl* derivative is very readily soluble in the common organic solvents, but crystallises from a large volume of light petroleum (b. p. 60—80°) in colourless, silky needles, m. p. 111·5° (Found: C, 67·9; H, 4·4. $C_{20}H_{16}O_6$ requires C, 68·2; H, 4·6%). The parent substance obtained by its hydrolysis crystallises from dilute alcohol in thin, colourless prisms containing water of crystallisation which is readily given up at 100°. The anhydrous substance has m. p. 219—220° (Found: C, 71·3; H, 4·6. $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5%).

7 : 8-*Dihydroxy*-2 : 3-*diphenylbenzo*-γ-*pyrone*.—This compound was prepared by benzoylation (20 hours) and subsequent hydrolysis of 2 : 3 : 4-trihydroxyphenyl benzyl ketone in the manner already described for the preparation of 5 : 7-dihydroxy-3-benzyl-2-phenylbenzo-γ-pyrone, and crystallised from alcohol in tiny, colourless needles, m. p. 297° (Found: C, 76·4; H, 4·1. $C_{21}H_{14}O_4$ requires C, 76·4; H, 4·3%). The *diacetyl* derivative crystallised from alcohol in fine, colourless, silky needles, m. p. 177—178° (Found: C, 72·2; H, 4·5. $C_{25}H_{18}O_6$ requires C, 72·4; H, 4·4%).

7 : 8-*Dihydroxy*-3-*benzyl*-2-*methylbenzo*-γ-*pyrone*.—Benzylgallaceto-

phenone (Dutta and Watson, J., 1912, **101**, 1241) was acetylated in the usual manner for 20 hours. The resulting *diacetyl* derivative crystallised from alcohol (charcoal) in almost colourless prisms, m. p. 126° (Found: C, 68·7; H, 4·9. $C_{21}H_{18}O_6$ requires C, 68·8; H, 5·0%). The parent substance obtained by its hydrolysis crystallised from very dilute alcohol in fine, colourless needles, which melt to a red liquid at 203—205° (Found: C, 72·0; H, 5·0. $C_{17}H_{14}O_4$ requires C, 72·3; H, 5·0%).

7 : 8-*Dihydroxy*-3-*benzyl*-2-*phenylbenzo*-γ-*pyrone* was prepared from benzylgallacetophenone in the same manner as the corresponding 2 : 3-diphenyl derivative described above. It crystallised from a large volume of acetic acid in pale yellow prisms, m. p. (when rapidly heated) 275—276° (Found: C, 76·4; H, 4·9. $C_{22}H_{16}O_4$ requires C, 76·7; H, 4·7%). This substance is very sparingly soluble in the usual organic solvents. The *diacetyl* derivative crystallises from alcohol in tiny, colourless, silky needles, m. p. 175—176° (Found: C, 72·6; H, 5·0. $C_{26}H_{20}O_6$ requires C, 72·9; H, 4·7%).

All these chromones derived from pyrogallol dissolve to pale yellow solutions in aqueous alkali hydroxides, none of which exhibits fluorescence (the same being true of the pale yellow solutions of the diacetyl derivatives in concentrated sulphuric acid); whilst their alcoholic solutions give a deep green colour with ferric chloride. The non-fluorescence of these substances is analogous to the cases of the *iso*brazilein and *iso*hæmatein salts and various benzopyrylium derivatives (Robinson, Crabtree, and Das, J., 1924, **125**, 211).

THE UNIVERSITY, MANCHESTER. [*Received, July 15th*, 1925.]

CCCXXI.—*The Formation and Stability of Associated Alicyclic Systems. Part II. The Formation and Disruption of Dicyclic Dihydroresorcinols.*

By ERNEST HAROLD FARMER and JOHN ROSS.

THE unsaturated cyclic ketones and ketonic esters of the five- and six-carbon series would appear to furnish attractive starting points for many chemical syntheses. In practice, however, owing to the transformations which accompany apparently simple operations, not only are the products other than those expected, but frequently it is extremely difficult to ascertain the course a given reaction has taken.

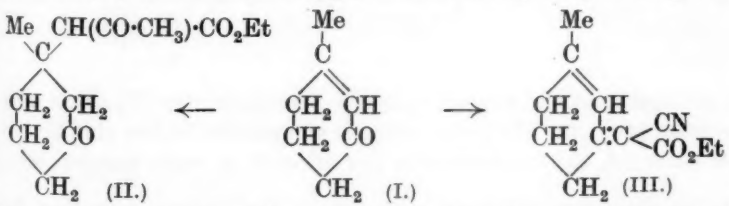
It has been recorded in the case of certain derivatives of dimethyl-*cyclo*pentenone (Farmer and Ingold, J., 1920, **117**, 1362; Farmer, Ingold, and Thorpe, J., 1922, **121**, 128) that the chemically active combination of double bond and carbonyl group may lead in cyclic

structures to a type of reactivity differing fundamentally from that observed in open-chain compounds, the effect of the spatial configuration and of the strained condition of the substituted carbon ring being such as to promote tautomeric valency exchange across the ring. Such a phenomenon might be expected to become manifest only under favourable structural and restrictive conditions, and, in the six-carbon series, where such an interchange would involve the establishment of "para" or "meta" bridge-valencies, and where the comparable restrictive conditions (the prevention of the functioning of a keto-enol system in the ring except at the expense

of valency adjustment across the ring) are exceedingly difficult of experimental realisation, no counterpart of the intra-annular tautomerism of the five-carbon series has yet been observed. In this connexion the uniplanar or multiplanar configuration is of moment; a multiplanar configuration, even although representing only changing contortions of the molecule and not giving rise to geometrical isomerides of the type obtained in the case of fused *cyclo*hexane rings (Hückel, *Nach. K. Ges. Wiss. Göttingen*, 1923, 43), would seem inevitably to affect intramolecular relationships.

In this series it is proposed to examine the relationships of the carbon pairs in a six-membered ring through their tendency to become united by bridges of one or more carbon atoms and in the present communication the ease of formation of 1 : 4-bridges consisting of the group $\cdot CH_2 \cdot CO \cdot$ is considered. The method employed is that of the Dieckmann condensation on the appropriate methyl-*cyclo*hexanone-acetic or -malonic esters.

The mode of reaction between 1-methyl-Δ^1-*cyclo*hexen-3-one (I) and esters of the malonic type appears from the literature to be anomalous. Thus according to Rabe (*Ber.*, 1904, **37**, 1671) reaction between the ketone and ethyl sodioacetoacetate yields an additive product (II) of the Michael type, which subsequently undergoes an



internal aldol condensation. With ethyl sodiocyanoacetate, however, it is stated (Knoevenagel and Mottek, *Ber.*, 1904, **37**, 4470) that reaction of the Knoevenagel type occurs leading to a methyl-

*cyclo*hexenylideneacetic ester (III), which also passes by internal condensation into a dicyclic compound.* Finally, towards ethyl sodiomalonate the ketone is stated to be indifferent (Vorländer and Gärtner, *Annalen*, 1898, **304**, 7).

Contrary to the last statement, ethyl sodiomalonate was found to react with the greatest facility, but the nature of the products varied with the experimental conditions used. When the condensation was effected at 100° in the presence of alcohol, the principal product was a high-boiling non-ketonic ester which, by reason of the difficulty attending its purification and that of its hydrolysis product, long resisted identification. It was ultimately identified as the compound (IV), and, as would be expected of such a substance,

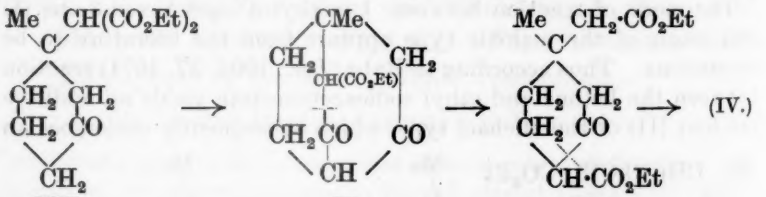
(IV.) $MeC(CH_2\cdot CH_2\cdot CH_2\cdot CO_2Et)(CH_2\cdot CO_2Et)(CH_2\cdot CO_2Et)$ $\qquad$ $MeC(CH_2\cdot CH_2\cdot CH_2\cdot CO_2H)(CH_2\cdot CO_2H)(CH_2CO_2H)$ (V.)

it yielded with sodium a cyclic keto-ester, presumably (VI), and its derived acid (V) an anhydro-acid, presumably (VII). The constitution of the tribasic acid (V) was finally established by synthesis

(VI.) $MeC(CH_2\cdot CH_2)(CH_2\cdot CO)(CH_2\cdot CO_2Et)(CH\cdot CO_2Et)$ $\qquad$ $MeC(CH_2\cdot CH_2\cdot CH_2\cdot CO_2H)(CH_2\cdot CO)(CH_2\cdot CO\cdot O)$ (VII.)

as recorded below, and the correctness of the formula assigned to the cyclic keto-ester (VI) followed from the subsequent oxidation of its derivatives.

The open-chain ester (IV) could have been produced only as the result of preliminary Michael addition followed in turn by internal condensation and two stages of ring fission, a procedure borne out

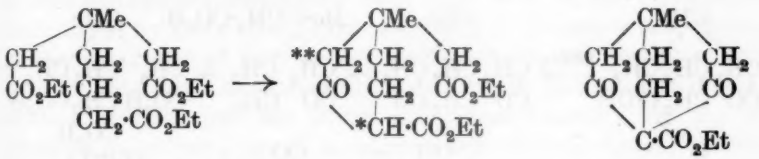


by the appearance of a quantity of the β-ketonic ester (X) along with the main product. In order to arrest the process before ring fission had occurred, the condensation was effected at room temperature.

* The alternative structures suggested for the dicyclic derivatives by Knoevenagel and Mottek involve internal condensations of such unusual type that the reinvestigation of the reaction between the cyclic ketone and ethyl cyanoacetate has been commenced.

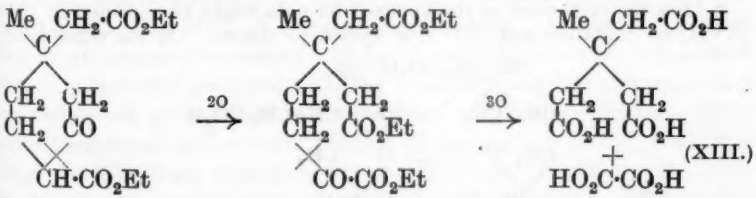
Among the products of reaction the original compound (VIII) and the open-chain ester (IV) could not be identified. Hydrolysis with mineral acids under special conditions gave a 50% yield of the methyl*cyclo*hexanoneacetic acid derived from (VI), but resinified the remainder of the material, regarded as representing the dicyclic 1 : 3-diketone (IX). The methyl*cyclo*hexanoneacetic acid produced was identical with that obtained by the direct condensation of β-methylpimelic-β-acetic ester (IV).

The attempted deliberate formation of the dicyclic diketone by the action of sodium on the ester (IV) failed so far as the main mass of material was concerned, the reaction proceeding only to the first stage (XI); nor could the pure ester (XI), derived from the acid (V), be converted into the dicyclic diketone.



(IV.) (XI.) (XII.)

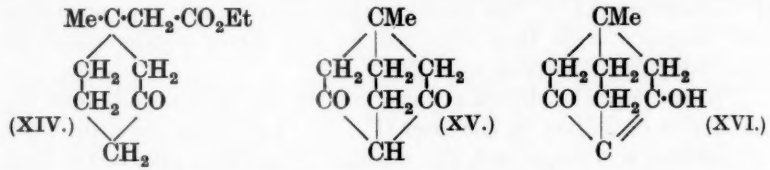
To the extent, however, of a few units per cent. there was obtained in the former reaction a crystalline quasi-acidic substance agreeing in composition with a dicyclodiketonic ester, but obtainable in insufficient amount to allow of the complete establishment of its constitution. The striking difference in the tendency towards further condensation of the esters (VIII) and (XI) may easily have arisen from the different distribution of the carbethoxyl groups. The non-formation in the latter case appears to have been due to the almost complete production of the *cis*-form of the monocyclic ester (XI) under the Dieckmann conditions, since the position of the carbethoxyl group at the carbon * rather than at ** became evident, so far as the main bulk of material was concerned, through the remarkably good yield of methylmethanetriacetic acid (XIII) and oxalic acid obtained on oxidation. This appears



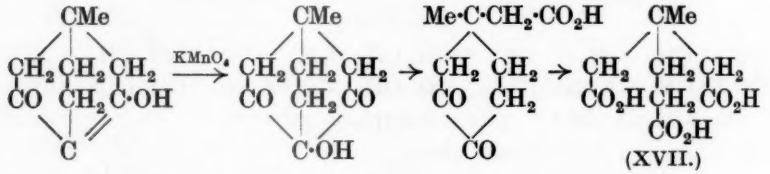
(XIII.)

the more probable in that the decarboxylated ester (XIV) reacted rapidly with sodium or even cold sodium ethoxide. Here, however,

owing to the instability * and viscous nature of the product the type of condensation effected is as yet uncertain. Although not completely homogeneous, the product would appear from many of its properties (p. 2366) to consist essentially of the dicyclic dihydroresorcinol (XV or XVI). Thus on oxidation it gave good yields of



the expected tribasic acid (XVII) and was reconverted on prolonged boiling with caustic alkali into the acid corresponding to (XIV).

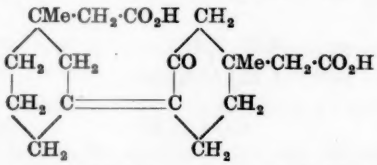


Nevertheless, in the absence of crystalline derivatives and in view of the high values obtained for the molecular weight by the cryoscopic method, the possibility of intermolecular condensation of the Knoevenagel type having taken place is not ruled out.†

Of the three tribasic acids produced during this investigation, one, methylmethanetriacetic acid (XIII), had already been synthesised by Thorpe and Wood (J., 1913, **103**, 1583), and a specimen was obtained by repeating their synthesis. The two homologues of this acid (IV and XVII) were obtained from ethyl lævulate and ethyl γ-acetobutyrate, respectively, by means of the Guareschi method of synthesis. The ketonic esters gave with ethyl cyanoacetate and

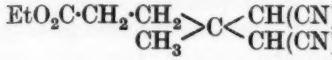
* The common dihydroresorcinols pass on attempted distillation into vitreous substances, and the only known dihydroresorcinol alkylated on the carbon between the carbonyl groups changes from a crystalline substance into a viscous oil on standing (Becker and Thorpe, J., 1922, **121**, 1303).

† Thus the compound of the annexed formula might be expected to yield (XVII) on oxidation and (XIV) on hydrolytic fission. On the other hand,



several undoubted examples of this type of condensation product have proved to be highly crystalline substances.

ammoniacal alcohol excellent yields of the ammonium salts of the ester imides (XVIII and XIX), which on hydrolysis yielded the



(XVIII.)

(XIX.)

required acids (XVII and IV).

EXPERIMENTAL.

1-*Methyl*-Δ^1-cyclo*hexen*-3-*one*.—Large quantities of this ketone were prepared by the method of Rabe and Rahm (*Annalen*, 1904, **332**, 13), dilute sulphuric acid (10%) being used for the hydrolysis of the methylenediacetoacetic ester. In view of the subsequent withdrawal by Rabe (*Ber.*, 1912, **45**, 2924) of his earlier description of the properties of pure methyl*cyclo*hexenone, the purity of the product obtained was thoroughly tested by the quantitative degree of its conversion into the oxime and semicarbazone. The use of alkali as hydrolysing agent, as suggested in the later paper, proved far less satisfactory than that of sulphuric acid. After a preliminary fractionation in a vacuum, the portion distilling at 199—202° at the ordinary pressure (through a short column) could be regarded as pure ketone.

A. *Condensation of Ethyl Sodiomalonate with Methyl*cyclo*hexenone*.

(a) *At* 100°. The ketone (1 mol.) was gradually added to a cold alcoholic solution of ethyl sodiomalonate (1 mol.), and the mixture heated on a steam-bath for 16 hours. The cooled product was poured on to ice and separated in the usual way into three portions, which were respectively neutral, quasi-acidic (soluble in caustic alkali but insoluble in sodium carbonate), and acidic in reaction. The latter two fractions were red oils giving purple colours with ferric chloride. They represented less than 10% of the total material and could not be resolved into pure compounds.

Ethyl β-*Methylpimelate*-β-*acetate*.—The neutral portion (above) constituted over 90% of the reaction product. In the crude state it gave an intense blue colour with ferric chloride, but after exhaustive fractionation the material distilled constantly at 200°/18 mm. as a colourless oil, giving then a faint colour with ferric chloride. Only after hydrolysis and re-esterification of the acid produced, could the ester be obtained completely pure (Found: C, 60·6; H, 8·75. $C_{16}H_{18}O_6$ requires C, 60·7; H, 8·9%). The yield was 65% of the theoretical.

The remainder of the crude neutral portion (b. p. 180—185°/18

mm.) consisted principally of ethyl 1-methyl*cyclo*hexan-3-one-4-carboxylate-1-acetate (below).

β-*Methylpimelic*-β-*acetic Acid*.—The corresponding ester was boiled for 8 hours with 15% hydrochloric acid. After neutralising the solution with alkali and boiling off the alcohol, the acid was obtained in almost quantitative yield by ethereal extraction of the cooled, reacidified liquid. Evaporation of the ether left an oil which rapidly solidified. Complete purification of the acid for analytical purposes was a laborious process owing to the presence of a trace of a second substance which crystallised with the acid. This difficulty, which caused many months' delay in the original identification of the acid, was not experienced with the acid synthesised from γ-acetobutyric ester (p. 2368). Repeated crystallisation from acetone–chloroform and ethyl acetate yielded the acid in colourless prisms, m. p. 123—124° [Found: C, 52·0; H, 6·9; *M* (tribasic), 234. $C_{10}H_{16}O_6$ requires C, 51·7; H, 6·9%; *M*, 232]. On heating the acid for 1½ hours with excess of acetyl chloride, *anhydro*-β-*methylpimelic*-β-*acetic acid* (VII) was obtained. It crystallised from benzene in long, transparent needles, m. p. 83° (Found: C, 55·8; H, 6·4. $C_{10}H_{14}O_5$ requires C, 56·05; H, 6·6%).

The pure *ethyl* ester was prepared by saturating an alcoholic solution of the acid at 0° with dry hydrogen chloride and distilling the product in a vacuum. It was obtained in almost quantitative yield as a colourless oil, b. p. 200°/18 mm. (Found: C, 60·8; H, 9·15. Calc., C, 60·7; H, 8·9%).

(b) *At room temperature*. Since the ketone would not react appreciably with an alcohol-free, ethereal suspension of ethyl sodiomalonate, the condensation was effected as in (a) except that the mixture was not heated; it was kept in a closed vessel for a week. On working up the material, negligible quantities of quasi-acidic and acidic substances were obtained.

Ethyl 1-*Methyl*cyclo*hexan*-3-*one*-4-*carboxylate*-1-*acetate*.—The neutral ester so obtained (86% theory), although consisting largely of the methylcarboxy*cyclo*hexanone-acetic ester (VI), could not be satisfactorily resolved into its constituents. It was obtained on distillation as a colourless oil, b. p. 175—190°/16 mm. After repeated fractionation, specimens were obtained (b. p. 182°/16 mm.) which gave correct figures on analysis (Found: C, 62·2; H, 8·2. Required for $C_{14}H_{22}O_5$, C, 62·2; H, 8·2) for the carboxy-acetic ester (VI) or the isomeric ethyl 1-methyl*cyclo*hexan-3-one-1 malonate (VIII). The presence of the latter ester, however, could not be demonstrated and all fractions gave intense colours with ferric chloride. The pure ester was readily obtained by the method described below (p. 2366).

Ethyl Ethane-$^{1:2}$*II*$^{1:4}$*-1-methylcyclohexa-3 : 5-dione-2-carboxylate.**—Although this substance could not be isolated in pure condition from the condensation product, its presence was probably responsible for the considerable amount of resinous material obtained on hydrolysis of the ester mixture. Boiling with alcoholic sodium ethoxide converted the mixture into ethyl β-methylpimelate-β-acetate.

1-*Methylcyclohexan-3-one-1-acetic Acid.*—This substance was obtained in small amount from the ester fraction, b. p. 180—185°/18 mm., derived from the condensation effected at 100°, but in much larger quantities from the product of condensation at 15°. The ester, after one distillation, was boiled with a mixture of equal volumes of alcohol and concentrated hydrochloric acid diluted with 2 volumes of water. After boiling for 3 hours, the excess of alcohol was expelled and refluxing continued for a further 7 hours. The cooled product was neutralised with sodium carbonate and extracted with ether. The mother-liquor was acidified with hydrochloric acid and re-extracted with ether. The oil thus isolated, on distillation, was obtained pure and colourless; b. p. 196°/15 mm., yield 60%. The acid passed on standing for some weeks into a solid, m. p. 37°. The *semicarbazone* was formed with considerable difficulty and did not crystallise well, thus rendering purification difficult. It separated from methyl alcohol as a white powder, m. p. 189° (Found: C, 52·2; H, 7·5. $C_{10}H_{17}O_3N_3$ requires C, 52·8; H, 7·5%). The *silver* salt was obtained as a white powder (Found: Ag, 38·8. $C_9H_{13}O_3Ag$ requires Ag, 39·0%).

Ethyl 1-*methylcyclohexan-3-one-1-acetate* was obtained by treatment of the silver salt of the acid with alcoholic ethyl iodide. It was a colourless oil, b. p. 147°/15 mm., which yielded no colour with ferric chloride (Found: C, 66·5; H, 9·2. $C_{11}H_{18}O_3$ requires C, 66·6; H, 9·15%). The ester could readily be converted into its *semicarbazone*, which separated from ether in colourless prisms, m. p. 158—159° (Found: C, 56·2; H, 8·2. $C_{12}H_{21}O_3N_3$ requires C, 56·4; H, 8·3%).

B. *Direct Condensation by the Dieckmann Method.*

General Method.—Sodium (2 atoms) was pulverised under xylene and the xylene replaced by a volume of benzene or toluene equal to that of the ester (1 mol.), which was immediately added. The whole was heated on a steam-bath until energetic reaction commenced. When this had subsided, heating was re-commenced and continued

* The nomenclature used for this and succeeding dicyclic compounds is that described in Part I of this series (J., 1920, **117**, 591).

until reaction was complete. The cooled product was treated with ice and extracted with ether. The mother-liquor was then acidified and extracted.

Intramolecular Condensation of Ethyl β-*Methylpimelate*-β-*acetate.*—The neutral ester obtained in 75% yield by the general method distilled as a colourless oil (b. p. 182°/15 mm.) which gave a deep purple colour with ferric chloride. This was pure *ethyl* 1-*methyl*-cyclo*hexan*-3-*one*-4-*carboxylate*-1-*acetate* (p. 2364) (Found: C, 61·9; H, 8·3. $C_{14}H_{20}O_5$ requires C, 62·2; H, 8·2%). This ester yielded no semicarbazone, but on hydrolysis by the method recorded above (p. 2365) yielded an acid identical in all respects (including the properties of its derivatives) with the methyl*cyclo*hexanoneacetic acid previously described. From the silver salt the ethyl ester (semicarbazone, m. p. 158—159°) was readily prepared. For the preparation of large quantities of this ester the foregoing method, in conjunction with the Guareschi synthesis (below), is especially suitable.

Ethyl Ethane-$^{1:2}$$\Pi^{1:4}$-1-*methyl*cyclo*hexa*-3 : 5-*dione*-2-*carboxylate.*—The portion of the condensation product which was soluble in caustic alkali but insoluble in sodium carbonate was distilled (b. p. 190—200°/18 mm.). The distillate deposited crystals which on recrystallisation from light petroleum were obtained in long, colourless needles, m. p. 111°. This substance did not immediately give a colour with ferric chloride; an intense colour developed after 10 minutes (Found: C, 63·7; H, 7·4. $C_{12}H_{16}O_4$ requires C, 64·1; H, 7·1%). Owing to the small amount of material available, the correctness of the constitution assigned could not be fully established.

Ethyl Hydrogen 1-*Methyl*cyclo*hexan*-3-*one*-4-*carboxylate*-3-*acetate.*—The acidic portion of the condensation product partly solidified. By treatment with ligroin the separation of the solid from the oily matter was possible. On recrystallisation from ligroin, the solid melted at 91° and gave an immediate colour with ferric chloride (Found: C, 59·4; H, 7·55. $C_{12}H_{18}O_5$ requires C, 59·5; H, 7·5%). Hydrolysis of the crude acid fraction gave a good yield of methylpimelic-acetic acid.

Intramolecular Condensation of Ethyl 1-*Methyl*cyclo*hexan*-3-*one*-1-*acetate.*—The small amount of neutral ester derived by condensing the cyclic ester (XI) with sodium according to the general method proved to be unchanged material. The large amount of acidic material was almost entirely soluble in sodium carbonate and gave no colour with ferric chloride. On distillation in a vacuum a portion passed over as a viscous, colourless oil (containing some methyl-*cyclo*hexanoneacetic acid), but the major portion would not distil

and set to a resinous mass on cooling. The undistilled substance readily gave a silver salt which on treatment with methyl iodide yielded an oil, only a portion of which passed over on distillation and from which no pure substance could be obtained. Numerous attempts to purify the acidic substance were without success, nor could crystalline derivatives be obtained. The composition and basicity corresponded approximately with that of *ethane*-$^{1:2}$$\Pi^{1:4}$-1-*methyl*-$\Delta^3$-cyclo*hexen*-3-*ol*-5-*one* (XVI). A similar product was obtained by using alcoholic sodium ethoxide instead of sodium. This material, after prolonged desiccation, gave in benzene solution molecular weight values almost double of that corresponding to formula XV or XVI. Boiling for some hours with caustic soda caused conversion into methyl*cyclo*hexanoneacetic acid.

C. *Oxidation of Cyclic Compounds.*

Oxidation of Ethyl 1-*Methyl*cyclo*hexan*-3-*one*-4-*carboxylate*-1-*acetate*.—To an ice-cold suspension of the ester in very dilute caustic potash, 3% potassium permanganate solution equivalent to about 5 atoms of oxygen was added drop by drop, with rapid stirring. After removal of the manganese, the solution was evaporated to small bulk and extracted with ether. From the concentrated ethereal solution an excellent yield of a sand-coloured acid separated. This was methylmethanetriacetic acid, which, after precipitation from concentrated aqueous solution by hydrogen chloride and finally crystallising from acetone–chloroform, separated in colourless prisms, m. p. 172° [Found: C, 46·8; H, 6·0; *M* (tribasic), 210. Calc., C, 47·0; H, 5·9%; *M*, 204]. This acid was compared directly with the acid synthesised by Thorpe and Wood's method (*loc. cit.*) and found to be identical.

From the aqueous mother-liquor an amount of calcium oxalate approximately equivalent to the organic acid was isolated.

Oxidation of the Product of Reaction of Sodium on Ethyl 1-*Methyl*-cyclo*hexan*-3-*one*-1-*acetate*.—The substance, dissolved in dilute sodium carbonate, was oxidised under conditions very similar to those described above. The intermediate oxidation products possessed considerable stability and the solution needed stirring for 1½ hours after addition of the necessary amount of permanganate (corresponding to 3 atoms of oxygen) was complete. After filtering and concentrating, the solution was acidified with hydrochloric acid. The intense bright red colour thus produced persisted for several days, but was instantly discharged by ammonia, only to reappear on acidification with acetic acid. Extraction of the acid liquor with ether yielded an oil which slowly deposited a crystalline acid.

This separated in small, colourless prisms, m. p. 148—149°, from acetone–chloroform [Found : C, 49·3; H, 6·55; *M* (tribasic), 212. $C_9H_{14}O_6$ requires C, 49·5; H, 6·5%; *M*, 218]. This acid was compared directly with a specimen synthesised from ethyl lævulate (Section D) and found to be identical.

D. *Guareschi Synthesis of Polycarboxylic Acids.*

β-*Methylpimelic*-β-*acetic Acid.*—Ethyl γ-acetobutyrate (8 g.), prepared by Bentley and Perkin's method (J., 1896, **69**, 1511), was mixed with ethyl cyanoacetate (11·3 g.). To the cold mixture, ammoniacal alcohol (25 c.c.) saturated at −10° was added. The product was kept at 0° in a tightly stoppered bottle for 2 days; inoculation with a crystal of an analogous imide then initiated crystallisation. Thus the ammonium salt (m. p. 97°) of an ester imide was obtained in good yield. From this the imide separated on acidification as a thick oil which soon solidified. More of the imide was obtained from the mother-liquor by removing the alcohol, without applying heat, and acidifying. It separated from dilute aqueous alcohol in long, transparent needles, m. p. 138—139° (Found : C, 57·3; H, 5·8; N, 14·9. $C_{14}H_{17}O_4N_3$ requires C, 57·7; H, 5·9; N, 14·4%).

The imide (2·5 g.) was mixed with 15 c.c. of concentrated sulphuric acid; when water (15 c.c.) was added, the imide dissolved. After 7 hours' boiling, hydrolysis was complete without carbonisation having taken place. Ethereal extraction of the cooled, diluted product yielded an oily acid which soon solidified in an evacuated desiccator (yield 2·1 g.). Recrystallisation from concentrated acetone–chloroform solution yielded colourless, well-defined prisms of β-methylpimelic-β-acetic acid, m. p. 124—125°. This m. p., differing by 1° from that recorded above, was not depressed by admixture of the two acids [Found : C, 51·7; H, 7·1; *M* (tribasic), 234. Calc., C, 51·7; H, 6·9%; *M*, 232].

β-*Methyladipic*-β-*acetic Acid.*—This acid was prepared from ethyl lævulate analogously to the preceding one. The crystalline ammonium salt (m. p. 136°) gave an excellent yield of the ester imide (XVIII), which separated from aqueous alcohol in long, transparent needles, m. p. 169° (Found : C, 55·6; H, 5·5; N, 15·8. Required for $C_{13}H_{15}O_4N_3$, C, 56·3; H, 5·4; N, 15·2%).

By hydrolysis of the imide with a mixture of equal volumes of sulphuric acid and water the acid was obtained. It was recrystallised from a mixture of equal volumes of acetone and chloroform, from which it separated in hard, colourless prisms, m. p. 148—149° (Found : C, 49·35; H, 6·4. Calc., C, 49·5; H, 6·5%).

The thanks of the authors are due to Professor J. F. Thorpe, F.R.S.; and to the Chemical Society for assistance in the purchase of materials through a grant made to one of them (J. R.).

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[*Received, March 17th,* 1925; *revised, August 17th,* 1925.]

CCCXXII.—*Applications of Thallium Compounds in Organic Chemistry. Part II. Titrations.*

By GEORGE HALLATT CHRISTIE and ROBERT CHARLES MENZIES.

AMONG new salts prepared by titration (see, *inter alia*, Menzies and Wilkins, J., 1924, **125**, 1148) are *thallous fumarate* and *thallous maleate*, which exhibit differences in properties similar to those displayed by the acids.

Tetrathallium tartrate, $C_4H_2O_6Tl_4$, prepared in alkaline solution, is sparingly soluble in water; the solution turns phenolphthalein pink, and the amount of acid required to discharge the colour corresponds to two equivalents of thallium. The salt may be recrystallised unchanged from a sufficiency of water; if, however, carbon dioxide be passed while heating, solution takes place more rapidly and the liquid on cooling deposits the characteristic needles of thallous carbonate. These facts indicate that two of the four thallium atoms are hydrolysable.

This salt does not appear to have been prepared before, as thallous tartrate has hitherto been made from the acid and thallous carbonate (Kuhlmann, *Compt. rend.*, 1862, **55**, 608; Carstanjen, *J. pr. Chem.*, 1867, **102**, 146; Lamy and des Cloizeaux, *Ann. Chim. Phys.*, 1869, **17**, 335; Glucksmann, *Z. Kryst. Min.*, 1894, **23**, 566). Carstanjen states that thallous tartrate has an alkaline reaction, but we find that tartaric acid may be accurately titrated with thallous hydroxide solution and phenolphthalein, the end-point being sharp.

In its somewhat sparing solubility, tetrathallium tartrate resembles the double tartrate of thallium and antimony (Kuhlmann; Lamy and des Cloizeaux; *loc. cit.*), and it is possible that it is the first example of a metallic hydroxy-acid complex formed by a univalent metal (see Wark, J., 1923, **123**, 1815).

An attempt to prepare tetrapotassium tartrate failed, normal potassium tartrate alone being obtained by concentration of a solution containing potassium hydroxide (4 equivs.) and tartaric acid (1 equiv.). Thallium compounds prepared on similar lines from lactic, malic, citric, and salicylic acids gave irregular analytical

results. β-Diketones, however, and phenols give thallium salts which resemble tetrathallium tartrate in the ease with which they can be prepared pure, and in the accuracy with which the thallium, hydrolysed by water, may be estimated by titration. These compounds are now described, as the usefulness of readily prepared, well-crystallised substances of this type is obvious. The crystalline forms are often characteristic and develop on mixing drops of the solutions, so that their possible application in micro-analysis is indicated. Of interest are the *thallous* salts of ethyl acetoacetate and of benzoylacetone, which resemble the thallous salts of acetylacetone and of acetonedicarboxylic ester in being readily soluble in organic solvents. Reactions of the above types of compound are under investigation and will be described in a later communication. Diphenyl ether, for instance, is formed by refluxing a solution of thallous phenoxide in iodobenzene, *o*-methoxybenzaldehyde has been obtained in 62% yield by heating thallium salicylaldehyde (Menzies and Wilkins, *loc. cit.*) under reflux with methyl iodide in benzene, and methyl stearate in quantitative yield from thallous stearate in the same way. The latter reactions as well as the former show that the resemblance between univalent thallium and the metals of both the A and the B sub-group of group 1 of the periodic table is not confined to inorganic chemistry.

Experimental.

Thallous Salts of Organic Acids.—These salts were prepared by titrating the acids with standardised thallous hydroxide solution and phenolphthalein, and were analysed after being filtered off and dried in a vacuum at 100°. The accuracy of the titrations is the same as in the cases of sodium and potassium hydroxides, the values for the equivalent weights of the acids generally being correct to three significant figures.

Thallous fumarate separates, when the solution obtained by titration is cooled, in white, elongated prisms, m. p. 268° (decomp.) (Found: Tl, 77·9. $C_4H_2O_4Tl_2$ requires Tl, 78·2%). It is sparingly soluble in water. *Thallous maleate* crystallises, on evaporation of its solution over sulphuric acid, in thick, white prisms, m. p. 164—166° (Found: Tl, 77·85. $C_4H_2O_4Tl_2$ requires Tl, 78·2%). It is readily soluble in water. *Thallous succinate* crystallises in irregular plates, m. p. 246—248°, on slow evaporation of its solution (Found: Tl, 77·6. $C_4H_4O_4Tl_2$ requires Tl, 77·9%). *Thallous phthalate* forms white prisms, m. p. 268—270° (Found: Tl, 70·8, 71·1. $C_6H_4O_4Tl_2$ requires Tl, 71·4%).

Holde and Selim (*Ber.*, 1925, **58**, 524) prepared thallous palmitate and oleate (Menzies and Wilkins, *loc. cit.*) and thallous stearate by

titrating alcoholic solutions of the acids with $N/10$-aqueous thallous hydroxide and recrystallising the precipitated salts from alcohol. By the use of Kahlbaum's purified acids and a more concentrated solution of thallous hydroxide the pure salts may be obtained in one operation as follows: 7·35 g. of stearic, 8·96 g. of palmitic, and 9·76 g. of oleic acid, each dissolved in 200 c.c. of warm alcohol, required 29·9 c.c., 40·43 c.c., and 39·9 c.c. of 0·864N-aqueous thallous hydroxide (theory, 29·95, 40·48, and 40·03 c.c. respectively). On concentration and cooling there were obtained 10 g. of thallous stearate (m. p. 119°), 14 g. of thallous palmitate (m. p. 115°), and 8 g. of thallous oleate (m. p. 78—82°) (Found: Tl, 42·1 for oleate, 41·55 for stearate, 44·3 for palmitate. Calc., Tl, 42·1, 41·9, 44·5% respectively).

The observation that thallous palmitate softens at 116—118° but does not melt completely at 170° (Menzies and Wilkins, *loc. cit.*, p. 1149) led to its examination by polarised light * between crossed nicols; it was then found that between the above temperatures the salt behaves as an anisotropic liquid. The stearate and oleate show similar changes (see Holde and Selim, *loc. cit.*).

The thallous tartrate obtained by slow evaporation of its solution prepared by titration was dried in air (Found: on drying in a vacuum for 2 hours at 100—110°, H_2O, 1·6; in dried salt, Tl, 73·2. Calc. for the hemihydrate,† H_2O, 1·6; for the dried salt, Tl, 73·4%). This salt has a neutral reaction when redissolved in water. The salt obtained by Carstanjen (*loc. cit.*), and described as having an alkaline reaction, contained according to his analysis a slight excess of thallium (73·74%); both observations point to contamination with thallous carbonate used in its preparation.

Tetrathallium tartrate is deposited whenever a solution containing tartaric acid and thallous thallium is made alkaline. (1) 12·5 G. (78% of the theoretical yield) were obtained from 2·5 g. of tartaric acid and four equivalents of thallous hydroxide solution (121·4 c.c. of approximately 0·55N), the first few drops of which in excess

* At the suggestion of Professor Lapworth.

† 2-Methylpyridine-3 : 4 : 6-tricarboxylic acid (Lawson, Robinson, and Perkin, J., 1924, **125**, 637) forms another of the few thallous salts containing water of crystallisation. 7·8 G. (theory 8·7) of the above salt were obtained from 2·35 g. of the acid (kindly supplied by Professor Robinson) as a white, crystalline powder which, on heating, charred without melting. After exposure to moist air to constant weight, it lost on subsequent heating at 140—145° 1·9% of its original weight. Another sample, dried to constant weight at 145°, gained 2·2% of its final weight on exposure to moist air till the weight was again constant (6 days) [Found in dried salt: Tl, 73·1 (as TlI), 73·2 (as Tl_2O_3). $C_9H_4ON_6Tl_3$ requires Tl, 73·4%. $C_9H_4ON_6Tl_3,H_2O$ requires H_2O, 2·1%]. By a coincidence, 2-methylpyridine-3 : 4 : 6-tricarboxylic acid and tartaric acid have the same equivalent weight.

produced a precipitate (Found: Tl, 84·2 as iodide, 42·5 by titration.* $C_4H_2O_6Tl_4$ requires Tl, 84·8%). (2) 5·86 G. (yield 87·6%, calculated on thallous hydroxide taken) were obtained from 1·77 g. of acid potassium tartrate and three times the amount of thallous hydroxide solution required to neutralise the salt (Found by titration: Tl, 42·55%). (3) 37 G. (yield 77%) were obtained from a hot solution of 7·5 g. of tartaric acid, 8 g. of sodium hydroxide, and 50·4 g. of thallous sulphate in 500 c.c. of water (Found: Tl, 84·7, 84·8 as iodide; 42·5, 42·8% by titration). (4) 3·2 G. were obtained from 6 g. of normal thallous tartrate hemihydrate and 50 c.c. of approximately 0·44*N*-sodium hydroxide solution (Found by titration: Tl, 42·3%). (5) 0·38 G. was obtained from 1·39 g. of thallium hydrogen tartrate and 27 c.c. of the same sodium hydroxide solution (Found by titration: Tl, 42·5%).

Decomposition by carbon dioxide. Tetrathallium tartrate (9·9 g.) only partly dissolved in 50 c.c. of boiling water; but on passing carbon dioxide dissolution was rapid and, on cooling, 3·7 g. of thallous carbonate crystallised. Hydrolysis of half the thallium with formation of carbonate requires 4·8 g. of thallous carbonate, which is appreciably soluble in water.

Comparative Estimations, by Titration and by Precipitation as Thallous Iodide, of Thallium in its Salts with β-Diketones and with Phenols.—Thallous ethyl acetoacetate. The pure *compound* (24·3 g.) separated in needles, m. p. 91—92°, when 100 c.c. of thallous hydroxide solution (27·5 g. of TlOH per 100 c.c.) were mixed with 16·2 g. of ethyl acetoacetate dissolved in a little alcohol. The substance is readily soluble in organic solvents (Found: Tl, 61·1 as iodide; 61·2 by titration. $C_9H_9O_3Tl$ requires Tl, 61·3%).

The thallous salt of benzoylacetone (6·3 g.) was obtained in long, yellow prisms, m. p. 103—105°, from 7·3 g. of benzoylacetone and the equivalent amount of thallous hydroxide solution. It is sparingly soluble in pure ether, but conveniently recrystallised from acetone (Found: Tl, 55·9 as iodide; 55·6 by titration. $C_{10}H_9O_2Tl$ requires Tl, 55·9%).

Thallous acetyl acetone (Kurowski, *Ber.*, 1910, **43**, 1078; Morgan and Moss, J., 1914, **105**, 195). Found: Tl, 67·0 as iodide; 66·9 by titration. Calc., Tl, 67·4%.

The thallous salt of acetonedicarboxylic ester (Menzies and Wilkins, *loc. cit.*). Found: Tl, 49·85 as iodide; 50·0 by titration. Calc., Tl, 50·5%.

Thallous salts of phenols. Pure thallous phenoxide, m. p. 231—

* Percentages of thallium given as "by titration" have been calculated on the basis of 0·02044 g. of thallium per c.c. of *N*/10-acid required to neutralise weighed amounts of the substances in question in aqueous solution.

235° (Kuhlmann, *Bull. Soc. chim.*, 1864, **1**, 333), crystallises in long needles on cooling the solution obtained by mixing equivalent weights of phenol in alcohol and of thallous hydroxide in hot water. Supersaturation occasionally occurs (Found: Tl, 69·1 as iodide: 68·7 by titration. Calc., Tl, 68·7%).

Thallous m-*tolyloxide*, m. p. 187°, crystallises pure when a hot solution of *m*-cresol in an equivalent quantity of aqueous thallous hydroxide is cooled [Found: Tl, 65·2 as iodide; 65·7 by titration (methyl-orange). C_7H_7OTl requires Tl, 65·6%].

o- and *p*-Cresol also give characteristic salts, that of *o*-cresol differing from the others in its greater solubility in water.

The thallous salt of resorcinol monomethyl ether (2·48 g.) was obtained in thin prisms, m. p. 146—148°, from 1·28 g. of resorcinol monomethyl ether and 8·1 c.c. of 1·27 *N*-thallous hydroxide solution (yield 73·5%) [Found: Tl, 62·25, 62·4 as iodide; 63·0 by titration (methyl-orange). $C_7H_7O_2Tl$ requires Tl, 62·4%].

The thallous salt of guaiacol (8·1 g.) was obtained from 5·7 g. of guaiacol and 36·1 c.c. of 1·27*N*-thallous hydroxide solution in stout, rhombohedral plates, m. p. 160—161° (yield 53·7%). This salt is much less soluble in water than the salt of resorcinol monomethyl ether (Found: Tl, 62·4, 62·25 as iodide; 63·0% by titration).

Thallous α-*naphthoxide*, m. p. 180—190°. On cooling a hot aqueous solution of this substance, obtained in the usual way as an amorphous precipitate, an emulsion was first produced which, examined by ordinary light under a microscope, appeared to consist of small globules suspended in the liquid. These were invisible in plane-polarised light between crossed nicols, crystals of stout, doubly refracting plates soon crystallised and the emulsion disappeared [Found: Tl, 58·25 as iodide; 58·6 by titration (methyl-orange). $C_{10}H_7OTl$ requires Tl, 58·8%].

The thallous salt of vanillin separates in branching needles, m. p. 193—201°, in almost theoretical yield when a weighed amount of vanillin, dissolved in a little alcohol, is added to an equivalent quantity of moderately concentrated thallous hydroxide solution (Found: Tl, 56·8, 57·0 as iodide; 57·0 by titration. $C_8H_7O_3Tl$ requires Tl, 57·5%).

The authors wish to thank Miss C. M. Fear for assistance with the analytical work. They also gratefully acknowledge grants from the Research Fund Committee of the Chemical Society and the Colston Research Committee.

UNIVERSITY OF BRISTOL. [*Received, July 10th*, 1925.]

CCCXXIII.—*The Reactions of Azoxy-compounds. Part I. The Action of Light.*

By WILLIAM MURDOCH CUMMING and GEORGE STRATON FERRIER.

ALTHOUGH much has been published on the preparation of azoxy-compounds, few attempts have been made to explore the reactions of this somewhat stable group. Scattered observations (notably by Knipscheer, *Rec. trav. chim.*, 1903, **22**, 1) indicate that one characteristic reaction of azoxy-compounds, their conversion into hydroxyazo-compounds under the influence of sulphuric acid, can also be brought about by the action of light. Knipscheer obtained *o*-hydroxyazobenzene, in poor yield (10·3%), and with much loss of material through volatilisation (39·7%), by exposing sheets of filter-paper impregnated with azoxybenzene to sunlight for 5 weeks. He further stated, as a result of experiments in boiling benzene and toluene, that the transformation took place satisfactorily only when the azoxybenzene was in the solid state. As this did not agree with observations made in this laboratory (Cumming and Steel, J., 1923, **123**, 2465; Cumming and Ferrier, J., 1924, **125**, 1108) on αα′- and ββ′-azoxynaphthalenes, and as it was further believed that the loss of azoxybenzene through volatilisation could be greatly reduced by carrying out the transformation in solution, it was decided to reinvestigate the subject.

By exposing solutions of azoxybenzene in various solvents to the light of a mercury vapour lamp, *o*-hydroxyazobenzene was obtained in fair yield, varying with the conditions. The best results (28·0%) for 50 hours' exposure were obtained in absolute ethyl alcohol, and the worst (7·7%) in benzene. Increase of temperature materially increased the loss of azoxybenzene through volatilisation, and only slightly improved the yield. The transformation also takes place in sunlight, but cannot be effected by ordinary electric light. In this connexion it is of interest that Cumming and Steel (*loc. cit.*) have found that exposure of αα′-azoxynaphthalene to sunlight or to the light of a mercury vapour lamp for a short period produced a red isomeride of the same melting point (127°); prolonged exposure, however, produced an azonaphthol melting at 224° (private communication). This change they formulate thus:

$$\underset{\text{Yellow azoxynaphthalene.}}{\text{R·N–N·R}} \;(\text{O}) \longrightarrow \underset{\text{Red isomeride.}}{\text{R·N:N·R}} \;(\text{O}) \longrightarrow \underset{\text{Azonaphthol.}}{\text{R·N:N·R·OH}}$$

We have also obtained hydroxyazo-compounds from 2 : 2′-, 3 : 3′-, and 4 : 4′-azoxytoluenes, 4 : 4′-dichloroazoxybenzene, and

2 : 2′-diamino-4 : 4′-azoxytoluene under similar conditions. 4 : 4′-Azoxyanisole, 4 : 4′-azoxyphenetole, and 4 : 4′-dinitroazoxybenzene reacted slightly or not at all. In the case of 2 : 2′-azoxytoluene products of widely different melting points were obtained according to whether the transformation was carried out in alcohol or benzene solution. The hydroxyazo-compounds were obtained as red needles of varying solubility in sodium hydroxide solution. In cases where we were able to determine the orientation, the hydroxyl group appears to enter the benzene nucleus in the ortho-position with respect to the azo-group.

Janovsky and Reimann (*Ber.*, 1889, **22**, 40, 1172) state that by fractionally crystallising the product from the action of zinc and sodium hydroxide on *p*-nitrotoluene they obtained an isomeric *p*-azoxytoluene melting at 75°, which they state can also be obtained by the oxidation of *p*-azotoluene with nitric acid. We have been unable to obtain this isomeride by either method, and have shown that it is not a solid solution of *p*-azo- in *p*-azoxy-toluene. Our work, therefore, indicates that the existence of this isomeride is extremely doubtful.

Experimental.

Azoxybenzene.—A. *Effect of ultra-violet light.* Azoxybenzene (5 g.), dissolved in 85% alcohol (500 c.c.) contained in a quartz flask and placed under a reflux condenser to reduce loss through volatilisation, was exposed for 50 hours to the light of a mercury vapour lamp. The alcohol was then distilled off and the red, crystalline residue dissolved in ether and exhaustively extracted with 8% sodium hydroxide solution (2 litres). The ethereal solution after extraction yielded 3·65 g. of azoxybenzene. The alkaline extract, after acidification with hydrochloric acid, was kept overnight and filtered. A yellow powder (1·05 g.), m. p. 76—78°, was obtained, which was completely volatile in steam (hence containing no *p*-hydroxyazobenzene) and after crystallisation from alcohol formed red needles, m. p. 82—83°. Bamberger (*Ber.*, 1900, **33**, 1939) gives for *o*-hydroxyazobenzene m. p. 82·5—83°.

The compound was further characterised by formation of the copper salt described by Bamberger, who does not, however, give details of the method for its preparation. This can best be accomplished by mixing equivalent quantities of an alcoholic solution of cupric chloride with a sodium ethoxide solution of the dyestuff, and leaving to crystallise. The salt melted at 223° (Bamberger gives m. p. 225—226°).

A control experiment was carried out by keeping a similar solution of azoxybenzene in the dark for 14 days and working up

similarly. Pure azoxybenzene was recovered quantitatively. A sample of *o*-hydroxyazobenzene in alcoholic solution was exposed to the lamp for 125 hours, and the product fractionally crystallised from alcohol. No change was apparent.

The yields (per cent. of *o*-hydroxyazobenzene after 50 hours' illumination) obtained with various solvents were: 85% EtOH, 20·5; 100% EtOH, 28·0; MeOH, 24; PrOH, 26·3; C_6H_6, 7·7; boiling 85% EtOH, 22·3.

Dilution of the 85% ethyl-alcoholic solution from 1% to 0·5% of the azoxy-compound left the yield practically unaltered (26·0, 24·6%), but increase of time of exposure to 100 and 200 hours raised the yield to 44·0% and 63·3% respectively.

B. *Action of sunlight.* On June 24th, 1924, a solution of 18 g. of azoxybenzene in 1300 c.c. of 85% alcohol was divided between (i) a quartz flask (500 c.c.), (ii) a glass flask of approximately the same dimensions as (i) but with thinner walls (500 c.c.), and (iii) a thick glass reagent bottle (300 c.c.), in the proportions indicated. The flasks having been corked, and luted with sealing wax, were clamped to a retort stand in such a way as to ensure equal illumination, and exposed on the roof of the College until September 24th, when they were taken in and worked up in a similar manner to the other experiments. From the solution in (i) were obtained 1·56 g. (31·2%); from the solution in (ii), 1·88 g. (37·2%); and from the solution in (iii), 1·00 g. (33·3%), of the hydroxyazo-compound. Further experiment showed, however, that when the light of a mercury vapour lamp was employed, a solution in glass was only one-half as much transformed as one in quartz.

C. *Action of electric light.* A metal-filament lamp was immersed in a solution of 7·5 g. of azoxybenzene in 750 c.c. of alcohol, and lit for 50 hours. The solution had then only slightly changed colour, and on working up yielded pure azoxybenzene quantitatively.

2 : 2′-*Azoxytoluene.*—2 : 2′-Azoxytoluene (3 g.), dissolved in 85% alcohol (300 c.c.) and illuminated for 50 hours by means of the mercury vapour lamp, on transference to ethereal solution and extraction with 8% sodium hydroxide yielded practically nothing. The ether was removed, and the red, crystalline product added to a solution of 5 g. of 2 : 2′-azoxytoluene in alcohol, also previously illuminated. The whole was then fractionally crystallised from alcohol. The less soluble fractions were identified as 2 : 2′-azoxytoluene, the more soluble ones after purification and distillation under reduced pressure (b. p. 164°/3 mm.) melted at 47·5—48·5° and formed orange-red needles giving a deep-red solution in alcohol (Found: N, 12·4. $C_{14}H_{14}ON_2$ requires N, 12·4%).

Sixteen grams of 2 : 2′-azoxytoluene were dissolved in 650 c.c.

of benzene and illuminated for 50 hours. The solution, which had turned deep red, was concentrated, and extracted with 8% sodium hydroxide solution, to which it yielded nothing. After removing the benzene, and shaking with sodium hydroxide solution for 3 days (with negative results), the product was fractionally crystallised from alcohol. Together with unaltered initial material, a very small amount of red needles, m. p. 92—93°, closely resembling in appearance the other hydroxyazo-compounds, was obtained, but not in sufficient quantity for analysis.

3 : 3′-*Azoxytoluene.*—This substance was prepared by the method of Buchka and Schachteback (*Ber.*, 1889, **22**, 834), with slight modification. The purification of the azoxy-compound from traces of the nitro-compound sufficient to prevent crystallisation proved difficult, but the following procedure gave satisfactory results. The reduction mixture was steam-distilled, and the residue extracted with ether. After removal of as much of the ether as possible by distillation, the product was taken up in absolute alcohol and the last traces of ether were removed by heating on the water-bath. On dilution with a few drops of water and cooling in a freezing mixture, crystals of 3 : 3′-azoxytoluene separated. Further purification by crystallisation from 85% alcohol presented no difficulty.

Two flasks containing, respectively, 5 g. and 1·55 g. of 3 : 3′-azoxytoluene dissolved in 500 c.c. of 85% alcohol were illuminated for 52 hours. On working up as in the case of azoxybenzene, 0·38 and 0·17 g. respectively were obtained of a yellow powder, which after recrystallisation from alcohol formed red needles, m. p. 61·5—62·5° (Found : N, 12·6. $C_{14}H_{14}ON_2$ requires N, 12·4%). 4-Hydroxy-3 : 3′-dimethylazobenzene melts at 115°, and 6-hydroxy-3 : 3′-dimethylazobenzene at 95°. Therefore this substance is probably 2-*hydroxy*-3 : 3′-*dimethylazobenzene.*

4 : 4′-*Azoxytoluene.*—*Preparation* : see p. 2378.

Action of light. 4 : 4′-Azoxytoluene (4·72 g.), dissolved in 85% alcohol (500 c.c.) and illuminated for 54 hours, was treated as in the case of azoxybenzene, 6 litres of 8% sodium hydroxide solution being necessary to complete the extraction. 3-Hydroxy-4 : 4′-azoxytoluene (yield 0·47 g., or 10%), m. p. 150—151°, and otherwise agreeing with Macpherson and Boord's description (*J. Amer. Chem. Soc.*, 1911, **33**, 1531), was obtained.

4 : 4′-*Azoxyanisole.*—4 : 4′-Azoxyanisole (4·34 g.), dissolved in alcohol (500 c.c.), was illuminated for 50 hours, the solution being kept boiling to retain the azoxy-compound in solution. On cooling, 3·21 g. of pure azoxyanisole separated out (m. p. after recrystallisation 116·7°, clearing point 134°). The united mother-liquors

were evaporated, and the residues dissolved in ether and extracted with 1 litre of 16% sodium hydroxide solution. An orange, alkaline extract was obtained, which turned red on acidification, depositing a minute crop of red crystals, melting after crystallisation at 121°, but in too small quantity for further examination. On evaporation of the ethereal solution a further quantity (0·5 g.) of *p*-azoxyanisole was obtained.

In a previous experiment a curious effect was observed whereby a solution which had been illuminated for 17 hours became deep green, almost black. On illumination for a further period of 11 hours this colour faded to orange.

4 : 4′-*Dichloroazoxybenzene.*—4 : 4′-Dichloroazoxybenzene (5 g.) dissolved in boiling 85% alcohol was illuminated for 50 hours at the boiling point. After working up in the usual way, making use of sodium hydroxide solution, a small yield of red crystals, m. p. 171—172°, was obtained (Found: N, 9·8. $C_{12}H_8ON_2Cl_2$ requires N, 9·5%).

2 : 2′-*Diamino*-4 : 4′-*azoxytoluene.*—Three solutions were illuminated, a 1% solution in alcohol, a solution of the hydrochloride in water, and a similar solution in water containing excess of hydrochloric acid. In each case the product was much contaminated with tar. After removal of this by boiling alcoholic solutions with animal charcoal, and fractionally crystallising from alcohol, small quantities of red needles, m. p. 210°, were obtained. Graeff (*Annalen*, 1885, **229**, 346) gives for a hydroxyazotoluidine obtained by the action of sulphuric acid on 2 : 2′-diamino-4 : 4′-azoxytoluene a melting point 212°.

Reported Isomerism of 4 : 4′-*Azoxytoluene.*—Samples of 4 : 4′-azoxy- and azo-toluene were prepared from *p*-nitrotoluene by the method of reduction by zinc dust and ammonium chloride applied by us to other nitro-compounds (Cumming and Steel, Cumming and Ferrier, *loc. cit.*). Exhaustive fractional crystallisations from acetic acid and from absolute alcohol of the mixtures of azoxy- and azo-toluene obtained gave no trace of any compound melting at or about 75°. Further experiments in which the method of reduction employed by Janovsky was followed in detail were similarly unsuccessful. The yield from the former reduction is 10% better than from the latter. The action of 3 parts of nitric acid (*d* 1·51) does not, in our hands, give a product melting at 75°, but a mixture of a red substance, m. p. 202°, probably tetranitroazotoluene (Janovsky, *Monatsh.*, 1888, **9**, 839), with a white substance, m. p. 153°. The formation of the latter is favoured by increase of time of nitration. As it was suspected that the substance melting at 75° might be a solid solution of azotoluene in azoxytoluene

(compare Hartley and Stuart, J., 1914, **105**, 309, for the case of azobenzene and azoxybenzene), a setting-point curve of mixtures of *p*-azo- and *p*-azoxy-toluene was prepared. This revealed, however, no irregularities. From the setting point, 69·95°, of the pure azoxy-compound, the curve rises fairly steeply to the point corresponding to 75° and 10% of the azo-compound; addition of azotoluene to the azoxy-compound, therefore, does not depress the setting point of the latter. The curve then rises, first with slight concavity (relative to the composition axis) to the point corresponding to 140° and 99% of the azo-compound, and then steeply to 143·4°, the setting point of the pure azo-compound. A 50% mixture has a setting point of 118·5°.

It is a pleasant duty for one of us (G. S. F.) to acknowledge his indebtedness to Messrs. Nobel Industries and to the Carnegie Trustees for scholarships during the tenure of which this work was carried out.

ROYAL TECHNICAL COLLEGE, GLASGOW. [*Received, July 6th*, 1925.]

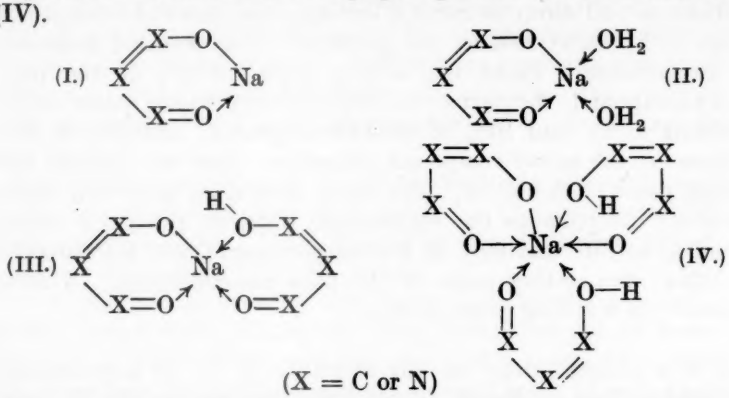
CCCXXIV.—*Co-ordinated Compounds of the Alkali Metals. Part II.**

By NEVIL VINCENT SIDGWICK and FREDERICK MASON BREWER.

THE discovery by Plant (*loc. cit.*) of the 4-covalent alkaline derivatives of ψ-indoxyl*spirocyclo*pentane made it of interest to see whether such derivatives were formed by the simpler compounds which give chelate rings with multivalent metals, such as β-diketones, β-ketonic esters, *o*-hydroxy-aromatic esters and aldehydes, and *o*-nitrophenols, the alkaline derivatives of which have hitherto been regarded as salts. It is possible that in some cases they are not salts, but covalent compounds with the metal forming part of a chelate ring (type I) as the replaceable hydrogen does in the original compound (Sidgwick and Callow, J., 1924, **125**, 532; Sidgwick, this vol., p. 907). The metallic atom might also assume a higher covalency of 4 or 6 (especially of 4, which is in general very stable); but it can only do so by forming addition compounds, either with the original or some similar organic compound, as happens with the ψ-indoxyl derivatives (III), or possibly by the co-ordination of two single molecules, as for example of water (II). Finally a third chelate ring

* Part I: Sidgwick and Plant, this vol., p. 209.

might be added in the same way, giving a 6-covalent metallic atom (IV).



It will be seen from what follows that there is considerable evidence for the existence of substances of the first of these types, and we have prepared numerous examples of the second and third, and some of the fourth.

1. *Simple Alkaline Derivatives.*

The alkaline derivative of, say, a β-diketone may either be a salt, or may have the metal covalently attached to oxygen. From the strong tendency of the alkali metals to ionise, we should not expect the compound to be covalent unless this made a further increase of stability possible, as through the closing of a chelate ring, which can happen with these compounds. Hence the alternative structures are (1) a salt and (2) a 2-covalent chelate compound. In the first case, the substance will have the usual properties of the salt of an organic acid: it will be insoluble in non-hydroxylic solvents and soluble in water, and on heating it is likely to decompose (char) without melting. In the second case, we may expect non-polar properties; a definite melting point, and greater solubility in organic solvents than in water.

The examination of the alkaline derivatives of substances of this kind shows that their properties are sometimes those of polar and sometimes those of non-polar compounds. They can behave in one of three ways, as the following examples show.

(1) When a benzene solution of ethyl malonate is treated with sodium, the sodium derivative separates as it is formed; it is quite insoluble in benzene, and when heated it chars without melting: it behaves as a salt.

(2) If ethyl methylmalonate is used, the sodium dissolves to form a clear solution, from which the compound does not immediately

separate even on concentration; but when once it has separated it is quite insoluble in benzene or toluene. (This might be ascribed to the formation of a colloidal solution, but the gradation of properties as we pass from class 1 to class 3 makes this improbable.)

(3) If ethyl acetoacetate is used, the sodium compound is found to melt to a clear liquid at 108°, and to be quite soluble in hot toluene.

These differences in behaviour suggest that the members of class 1 are always salts; that those of class 2 are non-polar chelate compounds when first produced, but on separation change into a more stable ionised form; whilst those of class 3 are stable in the non-polar form.

From our own observations and those recorded in the literature it appears that the majority of these compounds are of the first class. All the lithium derivatives we have prepared (including those of acetoacetic ester, acetylacetone, benzoylacetone, *o*-nitrophenol, 3-nitro-*o*-cresol, and quinizarin) are of this kind; they are insoluble in toluene and decompose on heating without fusion. Of the sodium derivatives, those of ethyl malonate, acetylacetone, ethyl cyanoacetate, methyl salicylate, salicylaldehyde, *o*-nitrophenol, 3-nitro-*o*-cresol, and quinizarin belong to this class. On the other hand, the sodium derivatives of the alkyl- and phenyl-malonic esters and (according to unpublished results of Dr. A. F. Titley) of 1-ketohydrindene-2-carboxylic ester, behave like that of methylmalonic ester (class 2), and the sodium salt of ethyl picrylmalonate (Jackson and Soch, *J. Amer. Chem. Soc.*, 1896, **18**, 133) does not separate on formation, although it is only very slightly soluble in benzene.

The sodium derivatives of acetoacetic ester, of ethyl ethylacetoacetate (Wislicenus, *Ber.*, 1874, **7**, 683), and of ethyl ethanetetracarboxylate belong to the third class, and are moderately soluble in non-hydroxylic solvents.

Of the comparatively few potassium derivatives examined, those of ethyl acetoacetate, ethyl cyanoacetate, and benzoylacetone are soluble to some extent in benzene and toluene, and melt at 106°, 135—137° and 146°, respectively, so that they belong to the third class. Where the sodium compounds are of the second kind, their potassium analogues appear to behave as salts (class I), and to be insoluble in benzene.

It is to be noticed that the replacement of the hydrogen attached to the middle carbon atom of the three (as in the esters of the alkylmalonic acids) promotes the stability of the non-polar form: this may be connected with its effect (on the Thorpe–Ingold theory) in closing up the chelate group.

There is thus some evidence of the existence of chelate compounds of 2-covalent sodium and potassium.

2. 4- *and* 6-*Covalent Derivatives* (*Addition Compounds*).

Many of these metallic derivatives which are insoluble in benzene and toluene readily dissolve in those solvents in presence of excess of the mother-substance. Thus it was found that sodium ethyl malonate, though quite insoluble in benzene, easily dissolved on warming in benzene containing an excess of malonic ester. On further heating, a gelatinous precipitate separated, consisting of the sodiomalonate. This suggests that a soluble addition compound is formed, which dissociates on heating. Evaporation of the solvent in the cold left a pasty mass from which no definite compound could be isolated. Similar behaviour was observed with ethyl methylmalonate, ethyl cyanoacetate, acetylacetone, benzoylacetone, and ethyl acetoacetate, though no precipitation took place on heating. It is not necessary that the parent substance should be present; for example, sodium acetylacetone will dissolve in a benzene solution of acetoacetic ester.

The more definite salts, such as the sodium derivatives of *o*-nitrophenol, salicylaldehyde, methyl salicylate, and the oximes of benzil, did not dissolve in benzene solutions of the parent substance, but were soluble in the parent substance itself. The solid obtained by the action of powdered sodium on excess of methyl salicylate, after drying on a porous plate, melted at 144° and contained 7·8% of sodium ($C_8H_7O_3Na,C_8H_8O_3$ requires Na, 7·2%), but on washing with ether it lost ester continuously; it may therefore be only a mixture, but is more probably an unstable compound. An analogous compound of salicylic acid, $C_7H_5O_3Na,C_7H_6O_3$, has been described by Hoitsema (*Z. physikal. Chem.*, 1898, **27**, 312): this we found not to be soluble as a whole in organic solvents: on prolonged treatment with benzene or ether it slowly lost salicylic acid, leaving a residue of sodium salicylate.

An attempt was made to prove the formation of a compound in solution by observing the depression of the freezing point of a solution of acetoacetic ester in benzene on addition of the sodium derivative; if the latter were wholly combined, its addition would cause no further depression. The available concentrations were limited by the separation of the sodium compound or of gelatinous products, but the results given in the following table indicate that some combination takes place, although it is by no means complete; the calculated values of the depression caused by the sodium compound are on the assumption that no combination occurs.

Per Cent. Ester	6·42	6·43	6·40	9·06	11·57
F. p. Depression	2·42°	2·42°	2·61°	3·62°	4·37°
Per Cent. Na Deriv.	2·56	1·52	0·872	0·828	0·585
Further Depression Calc.	0·90°	0·53°	0·31°	0·29°	0·20°
Further Depression Obs.	0·23°	0·18°	0·10°	0·10°	0·02°

Attempts to establish the formation of these compounds by means of solubility curves of the sodium derivative in the ester, either alone or in presence of toluene, were vitiated by the decomposition of the sodium derivative and its reaction with the ester at the temperatures required.

These facts taken together render it very probable that sodium is capable of forming 4-covalent compounds with substances of this kind; but for a definite proof the isolation of the products is needed.

Preparation of 4-Covalent Compounds.

Derivatives of Benzoylacetone.—The sodium derivative of benzoylacetone, $C_6H_5{\cdot}C(ONa){:}CH{\cdot}CO{\cdot}CH_3$, behaves as a salt: it has no definite melting point, and is quite insoluble in hydrocarbons. On recrystallisation from 96% alcohol, however, it became easily soluble in toluene. Analysis showed that the compound had taken up two molecules of water from the aqueous alcohol (Found: C, 54·2; H, 5·4; Na, 10·2. $C_{10}H_9O_2Na,2H_2O$ requires C, 54·55; H, 5·9; Na, 10·5%). It melts at 115°, with some preliminary loss of water; the water was identified by its b. p., and by its action on anhydrous copper sulphate. It is somewhat soluble in benzene and chloroform The solubility in hydrocarbons is in marked contrast to the behaviour of the original sodium derivative, and clearly shows that the compound is not a hydrated salt. The closure of the chelate ring is evidently due to the possibility of securing, by means of the water molecules, a stable covalency of 4 (formula II). The 96% alcohol contains just enough water to form the hydrate, but not enough to hydrolyse the original salt; on recrystallisation from water a small amount of the hydrate was obtained, but the greater part of the compound was hydrolysed. It was not found possible to prepare a double compound of sodium benzoylacetone and benzoylacetone; if water was carefully excluded, no product was obtained, and if water was present, the hydrate was formed.

A corresponding lithium compound was obtained, but it could not be freed from anhydrous salt (which is much less soluble in alcohol than its sodium analogue) by recrystallisation from alcohol. It was recrystallised from ethyl acetate, in which it is readily soluble (the anhydrous salt is insoluble). It forms lustrous, pearly plates (Found: Li, 3·4. $C_{10}H_9O_2Li,2H_2O$ requires Li, 3·4%).

Potassium benzoylacetone, which melts at 146° and is somewhat soluble in toluene, does not appear to form a stable hydrate.

Acetoacetic Ester.—A hydrate of the sodium derivative was prepared by Elion (*Rec. trav. chim.*, 1884, **3**, 240); by adding the ester to a suspension of excess of powdered sodium hydroxide in ether (in complete absence of moisture) he obtained a solution of the sodium derivative

in ether (presumably containing a non-polar compound with the ether), from which the hydrate was precipitated on adding a few drops of water. He describes this as a monohydrate, but his analyses are not very accurate. We found that it is very difficult to avoid the simultaneous precipitation of the anhydrous form, while the hydrate itself is very unstable. A freshly prepared specimen, precipitated by very vigorous stirring with a slight excess of water, melted at 102° and was completely soluble in benzene (the anhydrous salt melts at 108° and is practically insoluble in benzene, although it dissolves in hot toluene) (Found: C, 38·6; H, 6·2; Na, 12·75. $C_6H_9O_3Na,2H_2O$ requires C, 38·3; H, 6·6; Na, 12·2%). Although not quite pure, the compound is evidently the dihydrate. On standing, it decomposes, finally giving a substance of m. p. 82°, insoluble in benzene, which is also obtained by adding excess of water to Elion's solution of the sodium derivative; from its analysis it appears to be the dihydrate of sodium acetoacetate (Found: C, 31·0; H, 6·1; Na, 14·5. $C_4H_5O_3Na,2H_2O$ requires C, 30·0; H, 5·6; Na, 14·4%). This is confirmed by the fact that whilst the aqueous solution of the original dihydrate when acidified becomes turbid (from separation of ester), that of this product remains clear but evolves carbon dioxide. De Forcrand (*Ann. Chim.*, 1895, **5**, 405) obtained similar results. In the same way, Thorpe (J., 1900, **77**, 923) found that an aqueous solution of the sodium derivative of cyanoacetic ester is converted on evaporation to dryness into sodium cyanoacetate without any intermediate alkaline reaction. It is probable that the chelate form of the ester hydrate hydrolyses directly to the chelate isomeride of the salt hydrate.

Acetylacetone.—The sodium derivative was converted by recrystallisation from aqueous alcohol, acetone, or ethyl acetate into a hydrate; pearly plates, giving off water on heating, soluble in ethyl acetate (in which the anhydrous compound is insoluble), but not soluble in toluene. Very unstable: a specimen recrystallised from alcohol and ethyl acetate gave C, 35·8; H, 6·8; Na, 14·1; another specimen gave Na, 14·5 ($C_5H_7O_2Na,2H_2O$ requires C, 38·0; H, 7·0; Na, 14·55%). The potassium derivative is similar (Found: K, 23·0. $C_5H_7O_2K,2H_2O$ requires K, 22·4%); it rapidly decomposes, being apparently hydrolysed by its own water.

No lithium compound could be prepared.

Methyl Salicylate.—Only the lithium derivative forms a stable hydrate, produced on crystallisation from aqueous alcohol; it separates in plates, soluble in ethyl acetate (from which they were recrystallised) and in toluene (Found: Li, 3·8. $C_8H_7O_3Li,2H_2O$ requires Li, 3·6%). On heating, it loses water gradually, and finally melts at about 278°.

Salicylaldehyde.—Lithium compound. A solution of lithium hydroxide added to the aldehyde immediately precipitates the yellow, crystalline dihydrate: glistening, yellow plates (from alcohol), soluble in toluene, forming a colourless solution (Found: C, 50·5; H, 5·3; Li, 4·4. $C_7H_5O_2Li,2H_2O$ requires C, 51·2; H, 5·5; Li, 4·3%). It gives off water on heating, and melts indefinitely at about 228°.

Sodium compound. Hantzsch (*Ber.*, 1906, **39**, 3089) found that even with excess of sodium ethoxide salicylaldehyde forms an "acid salt"—an addition product of a molecule of the aldehyde and one of the simple salt. We found that this compound on washing with warm solvents gradually reverts to the simple salt (Found: Na, 15·9. $C_7H_5O_2Na$ requires Na, 16·0%); but by washing with cold ether it could be obtained pure (Found: Na, 8·7. $C_7H_5O_2Na,C_7H_6O_2$ requires Na, 8·6%); the same compound (Found: Na, 8·8%) separates from an alcoholic solution of the simple sodium salt to which an excess of the aldehyde has been added.

Potassium ethoxide was found by Hantzsch to behave in the same way, except that excess of it destroys the complex.

These double compounds are yellow, crystalline substances, slightly soluble in toluene, forming yellow solutions (the simple sodium and potassium derivatives are insoluble in toluene); they dissociate on heating in the solid state, and also in solution except in presence of excess of the aldehyde. Thus among the salicylic derivatives it is only with lithium that the monochelate hydrated form is produced; the sodium and potassium salts of the aldehyde give the dichelate form (formula III), corresponding to the ψ-indoxyl compounds. These differences no doubt depend on the relation between the strain in the ring and the size of the metallic atom.

o-Nitrophenol.—The ease with which salicylaldehyde forms chelate addition products with its salts suggested that it might do so also with other similar alkaline salts, such as those of the nitrophenols; and this was found to be so. The bright red sodium *o*-nitrophenoxide is a definite salt, soluble in water and hot alcohol, insoluble in toluene or ether. If salicylaldehyde is added to the solid salt the red colour at once disappears, the aldehyde is absorbed, and a bright yellow substance produced. After washing with ether, this has the composition of an addition compound of the salt and the aldehyde (Found: Na, 8·4. $C_6H_4O_3NNa,C_7H_6O_2$ requires Na, 8·1%). It dissolves in toluene on warming to form a yellow solution, which on further heating loses its colour and deposits the red sodium *o*-nitrophenoxide; excess of aldehyde prevents this dissociation. The same change occurs on heating the dry solid. No similar compound is formed from sodium *p*-nitrophenoxide. The substance evidently has the dichelate structure (III).

When sodium *o*-nitrophenoxide is crystallised from alcohol containing excess of salicylaldehyde, yellow, feathery crystals separate, mainly consisting of this substance, but with rather a high sodium content (9·3%) owing to some sodium salicylaldehyde and free nitrophenol having been formed: the latter has no tendency to form an addition compound, and remains in solution.

The yellow compound cannot be a mixture of nitrophenol and sodium salicylaldehyde, since its composition does not change on washing with ether.

Lithium forms no corresponding compound; the yellow crystals which were produced were found to be impure dihydrate of lithium salicylaldehyde.

Potassium *o*-nitrophenoxide in the anhydrous state is red, but it easily takes up water to form an orange hydrate, $2C_6H_4O_3NK,H_2O$ (Fritzsche, *Annalen*, 1859, **110**, 153; Frazer, *Amer. Chem. J.*, 1903, **30**, 309). This hydrate is slightly soluble in toluene, in which the red salt is quite insoluble. Either form yields with salicylaldehyde an ochre-yellow compound which is difficult to purify. When freshly made, it contained 13·8% of metal ($C_6H_4O_3NK,C_7H_6O_2$ requires K, 13·0%); it rapidly became discoloured, and after recrystallisation from alcohol contained excess of potassium, owing, no doubt, to interaction between the aldehyde and the salt.

3-*Nitro*-o-*cresol*.—This gave very similar results. The dry sodium salt changed from red to yellow on addition of salicylaldehyde, and the product after washing and drying gave Na 7·4% ($C_7H_6O_3NNa,C_7H_6O_2$ requires Na, 7·7%). The potassium salt absorbed a large excess of the aldehyde (possibly forming a 6-covalent derivative), but no definite compound could be isolated. When the lithium salt of the nitrocresol was recrystallised from an alcoholic solution of the aldehyde, only the dihydrate of lithium salicylaldehyde was obtained.

When acetylacetone was substituted for salicylaldehyde, no substance of this type was produced; either no reaction took place, or the alkaline salt of acetylacetone was formed.

Quinzarin.—The derivatives of 1-hydroxyanthraquinone can form chelate rings with the multivalent metals of the same type as those given by the β-diketones, and their lakes are recognised as chelate compounds (Werner, Morgan). Quinizarin (1 : 4-dihydroxyanthraquinone) was selected as having each hydroxyl in the proper position for chelation with a quinone oxygen. Its alkaline salts (which have two atoms of metal in the molecule) are not easy to purify, as they are somewhat insoluble, and easily hydrolyse with separation of quinizarin. They are best recrystallised from solutions containing excess of alkali. The lithium salt is

reddish-purple, the sodium and potassium salts are deep blue-purple.

When the sodium salt was treated with salicylaldehyde it turned brown, and after standing for 24 hours and washing with ether containing salicylaldehyde, a salmon-pink solid was left. It is decomposed by organic solvents with separation of the purple salt, but it is remarkable that it can be heated under water without any sign of hydrolysis. Analysis showed that this compound is formed by the addition of four molecules of salicylaldehyde to one molecule of the disodium salt (Found: C, 64·3; H, 4·0; Na, 6·1. $C_{14}H_6O_4Na_2,4C_7H_6O_2$ requires C, 65·3; H, 3·9; Na, 6·0%): an addition compound formed from 1 mol. of a monosodium salt and one of the aldehyde would have almost the same composition (C, 65·6; H, 3·4; Na, 6·0), but that it cannot have this formula is shown by its method of preparation, and is confirmed by the composition of the lithium compound (below).

The potassium compound was made in the same way, and had very similar properties (Found: K, 9·7. $C_{14}H_6O_4K_2,4C_7H_6O_2$ requires K, 9·7%).

These are the first recognised 6-covalent compounds of the alkali metals. If their formulation is correct, lithium cannot form an analogous compound, since its covalency is limited to 4; the salt can therefore only take up one molecule of the aldehyde for each lithium atom. The lithium compound was made in the same way as those of sodium and potassium, and has very similar properties. Analysis showed that it has the expected composition (Found: Li, 2·7. $C_{14}H_6O_4Li_2,2C_7H_6O_2$ requires Li, 2·8%).

We are indebted to Messrs. Brunner Mond and Co. for a grant from which part of the expenses of this research were met.

DYSON PERRINS LABORATORY, OXFORD. [*Received, August 7th*, 1925.]

CCCXXV.—*Studies in the Configuration of αα′-Dibromodibasic Acids. Part IV. The αα′-Dibromoglutaric Acids.*

By HARRY RAYMOND ING and WILLIAM HENRY PERKIN, jun.

THE previous sections of this research dealt with the determination of the configurations of the αα′-dibromoadipic acids (J., 1921, **119**, 1393; 1924, **125**, 1492) and of the αα′-dibromosuccinic acids (J., 1924, **125**, 1814). The present communication contains the results of similar investigations with the αα′-dibromoglutaric acids.

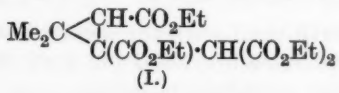
The dibromination of glutaric acid yields a mixture of two isomeric αα′-dibromoglutaric acids, one of which melts at 170° and

the other at 142° (Ingold, J., 1921, **119**, 312). The same two acids had previously been obtained by Thiele (*Annalen*, 1901, **314**, 305) by the oxidation of the *cis*- and *trans*-forms of 1 : 4-dibromo-2 : 3-dihydroxy*cyclo*pentane, the *cis*-form yielding the high-melting and the *trans*-form the low-melting acid; from this result Thiele concluded that the acid, m. p. 170°, was the *meso*-isomeride and the acid, m. p. 142°, the racemic acid. Ingold (*loc. cit.*) has brought forward evidence, based on the conversion of the dibromoglutaric acids into the corresponding dihydroxyglutaric acids, which supports Thiele's conclusions.

The ethyl esters of the αα′-dibromoglutaric acids are obtained as a liquid mixture of the *meso*- and *dl*-isomerides when the dibrominated glutaryl chloride is poured into ethyl alcohol, and this mixture cannot be separated into its components with certainty. One of the methyl esters, however, *viz.*, that of the dibromoglutaric acid, m. p. 170°, melts at 45°, whereas that of the acid, m. p. 142°, is a liquid, so that these esters can be obtained separate.

The dibromoglutaric esters were converted by heating with sodium iodide in alcohol into the corresponding di-iodo-esters. *Methyl di-iodoglutarate* was found to exist in a solid form, m. p. 75°, and a liquid form.

It was thought possible that the condensation of ethyl αα′-dibromoglutarate with 2 mols. of ethyl sodiomalonate might proceed in either or both of two ways, leading to a *cyclo*butane or to a *cyclo*propane ester. Thus trimethylene dibromide with ethyl sodiomalonate yields *cyclo*butanedicarboxylic ester, but the ββ-disubstituted αα′-dibromoglutaric esters which have been investigated yield only *cyclo*propane derivatives. αα′-Dibromo-ββ-dimethylglutaric ester, $CO_2Et{\cdot}CHBr{\cdot}CMe_2{\cdot}CHBr{\cdot}CO_2Et$, was found by Perkin and Thorpe (J., 1901, **79**, 729) to yield not the expected *cyclo*butane ester, but only the *cyclo*propanemalonic ester (I), which by the further action of sodium ethoxide gave rise to the yellow sodium derivative (II) of ethyl ketodimethyl*bicyclo*pentanetricarboxylate. Similar results were obtained by Ingold and Thorpe (J., 1919, **115**, 320) during the investigation of the action of ethyl sodiomalonate on αα′-dibromo*cyclo*hexane-1 : 1-diacetic ester.



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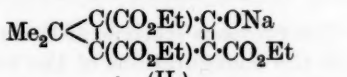

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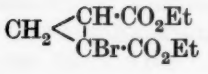

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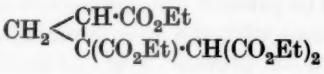

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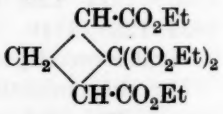


(V.)

The product of the condensation of αα′-dibromoglutaric ester with sodiomalonic ester might be either *cyclo*propane-1 : 2-dicarboxylic-1-malonic ester (IV), derived from the intermediate 1-bromo-*cyclo*propane-1 : 2-dicarboxylic ester (III), or *cyclo*butane-1 : 2 : 2 : 3-tetracarboxylic ester (V). Actually both types of ring formation take place. The product of the condensation of ethyl dibromoglutarate * with ethyl sodiomalonate in alcoholic solution consisted of unchanged ethyl malonate, ethyl bromo*cyclo*propanedicarboxylate (III), and an oil of the composition $C_{16}H_{24}O_8$. The bromo*cyclo*propane ester was identified by hydrolysis to 1-bromo*cyclo*propane-1 : 2-dicarboxylic acid, m. p. 175°, first described by Ingold (*loc. cit.*, p. 314). The oil $C_{16}H_{24}O_8$ was shown to be *ethyl* cyclo*butane-tetracarboxylate* (V) by the following facts : it did not yield a methyl derivative when digested with sodium ethoxide and methyl iodide and therefore did not contain a hydrogen atom replaceable by sodium ; and on hydrolysis with hydrochloric acid it was converfed into a mixture of the *cis*- and *trans*-forms of *cyclo*butane-1 : 2 : 3-tricarboxylic acid, first obtained by Goldsworthy and Perkin (J., 1914, **105**, 2665). The yield of ethyl *cyclo*butanetetracarboxylate was not more than 40—50% of the theoretical and the bromo*cyclo*propane ester represented only a small fraction of the original dibromo-ester. The red aqueous solution left after extraction of the oily product of the reaction contained the remainder of the product and on acidification it deposited a thick, red oil which could not be distilled owing to decomposition, but which on analysis gave figures corresponding to $C_{14}H_{18}O_7$, which formula differs from that of the *cyclo*butane ester, $C_{16}H_{24}O_8$, by C_2H_6O. It is difficult to see how the *cyclo*butane ester (V) could lose alcohol under the conditions of the experiment, but the *cyclo*propanemalonic ester (IV) might do so with the formation of the bridged-ring ester (VI), and although the ester of formula (IV) was not actually isolated, it seems probable that it would result from the action of sodiomalonic ester on the bromo*cyclo*propane ester (III) and that it would easily lose alcohol under the conditions of the experiment with the formation of the ester (VI) and thus escape isolation.

In order to test this view, ethyl bromo*cyclo*propanedicarboxylate (III) was condensed with ethyl sodiomalonate. No *cyclo*propanemalonic ester (IV) was isolated, but the aqueous extract of the reaction product yielded on acidification a thick, red oil which, after purification by solution in alkali and reprecipitation, had the composition $C_{14}H_{18}O_7$ and was evidently identical with the substance described above.

* Unless otherwise stated, the ethyl and methyl dibromoglutarates used in these condensations were mixtures of the *meso*- and *dl*-isomerides.

This experiment was repeated, using *methyl* 1-*bromo*cyclo*propane*-1 : 2-*dicarboxylate* and methyl sodiomalonate, a pale yellow, crystalline *sodium* derivative (VII) being obtained. This substance is

(VI.) $CH_2<\begin{matrix}C(CO_2Et)\cdot CO\\ C(CO_2Et)\cdot CH\cdot CO_2Et\end{matrix}$ $CH_2<\begin{matrix}C(CO_2Me)\cdot C\cdot ONa\\ C(CO_2Me)\cdot C\cdot CO_2Me\end{matrix}$ (VII.)

(VIII.) $CH_2<\begin{matrix}C(CO_2Me)\cdot CO\\ C(CO_2Me)\cdot CH\cdot CO_2Me\end{matrix}$

fairly soluble in water, the neutral solution giving a red colour with ferric chloride. When the aqueous solution is acidified, a solid is precipitated which after recrystallisation melts at 200°, has the composition $C_{11}H_{12}O_7$, and in our view is most probably methyl keto*bicyclo*pentanetricarboxylate (VIII).

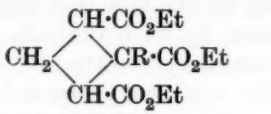
If this view is correct, this substance has a special importance, because it is the parent substance of ethyl ketodimethyl*bicyclo*pentanetricarboxylate discovered by Perkin and Thorpe (*loc. cit.*), which has been the subject of so much important investigation at the hands of Professors Thorpe and Ingold and their collaborators. The substance described by us is being submitted to a detailed examination in Professor Ingold's laboratory.

It is evident, therefore, that in the condensation of dibromoglutaric ester with sodiomalonic ester two reactions take place simultaneously, the one leading to a *cyclo*butane and the other to a *cyclo*propane ester. In alcoholic solution these two reactions proceed to about equal extents, but in the absence of alcohol, *e.g.*, in benzene solution, the *cyclo*butane ring formation predominates, the yield of *cyclo*butane ester rising to 70—80% of the theoretical.

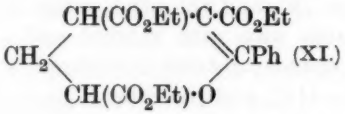
Ethyl dibromoglutarate was also condensed with the sodium derivatives of cyanoacetic, benzoylacetic, and acetoacetic esters. With ethyl sodiocyanoacetate in alcoholic solution, a 70% yield of *ethyl* 2-*cyano*cyclo*butane*-1 : 2 : 3-*tricarboxylate* (IX) was obtained, together with a small amount of ethyl bromo*cyclo*propanedicarboxylate. There was no evidence of the formation of a bridged-ring ester. The cyano*cyclo*butane ester (IX) on hydrolysis gave a mixture of the *cis*- and *trans*-modifications of *cyclo*butane-1 : 2 : 3-tricarboxylic acid.

The condensation of dibromoglutaric ester with ethyl sodiobenzoylacetate might give rise either to a benzoyl*cyclo*butane ester (X) or to a six-membered heterocyclic ester (XI). Actually *ethyl* 2-*benzoyl*cyclo*butane*-1 : 2 : 3-*tricarboxylate* (X) is formed to the extent of 30% of the theoretical, as was shown by its hydrolysis to benzoic acid and *cyclo*butanetricarboxylic acid. The other

products of the reaction were unchanged ethyl benzoylacetate and ethyl bromo*cyclo*propanedicarboxylate (III).

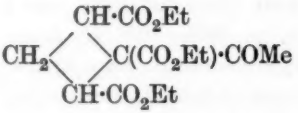


(IX, R=CN; X, R=COPh.)



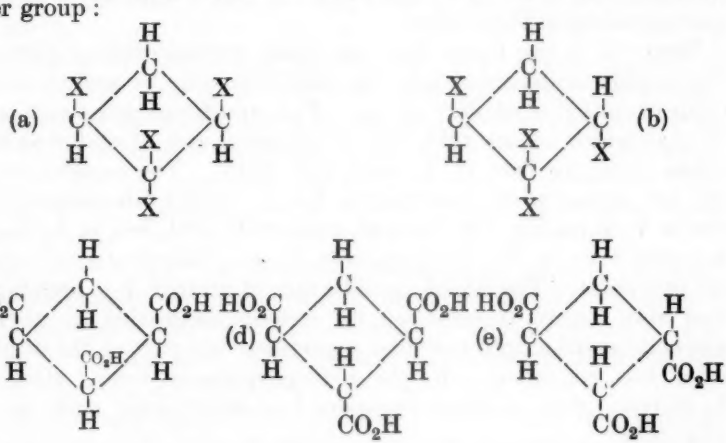
(XI.)

(XII.)



Similar results were obtained in an investigation of the action of dibromoglutaric ester on ethyl sodioacetoacetate, *ethyl* 2-*aceto*-cyclo*butane*-1 : 2 : 3-*tricarboxylate* (XII) being formed in about 30% yield. Attempts to hydrolyse the benzoyl- and acetyl-*cyclo*butane esters so as to obtain the corresponding acyl-*cyclo*butane acids were not successful, the acyl groups being removed by alcoholic potash even in the cold.

The ethyl dibromoglutarate used in all the condensations described above was a mixture of the *meso*- and *dl*-isomerides and consequently it was important to discover whether ethyl *cyclo*-butanetetracarboxylate formed from it was also a mixture. That this ester can exist as two stereoisomerides will be obvious from a consideration of the figures set out below, where X represents the ester group :



(a) represents a non-resolvable *meso*-form which would on hydrolysis and loss of carbon dioxide yield either or both of the two possible *meso*-forms of *cyclo*butane-1 : 2 : 3-tricarboxylic acid (c and d). (b) represents a racemic form which on hydrolysis and loss of carbon dioxide could give rise only to the racemic form (e)

of *cyclo*butanetricarboxylic acid. That the *cyclo*butane ester obtained in these condensations was actually a mixture of the two possible forms was made probable by the fact that two *cyclo*butanetricarboxylic acids were obtained by its hydrolysis, and it was confirmed by employing methyl dibromoglutarate with methyl sodiomalonate; two forms of *methyl* cyclo*butanetetracarboxylate* were then obtained, one a solid, m. p. 78°, and the other a liquid, b. p. 193—195°/15 mm. In the same way with methyl sodiocyanoacetate, two forms of *methyl cyano*cyclo*butanetricarboxylate* were obtained, one a solid, m. p. 111—112°, and the other a liquid, b. p. 195°/11 mm.

The *meso*- and *dl*-isomerides of methyl dibromoglutarate can be obtained separately in the pure state, since one of them is a solid (see p. 2393), so that it was important to discover whether each of the pure isomerides gave only one *cyclo*butane ester or a mixture of the two possible forms. The pure solid and liquid forms of methyl dibromoglutarate were separately condensed in benzene solution with methyl sodiomalonate and in each case a mixture of the two modifications of methyl *cyclo*butanetetracarboxylate was obtained. Similarly with methyl sodiocyanoacetate in alcoholic solution, a mixture of the two forms of methyl cyano*cyclo*butanetricarboxylate was obtained from both the solid and the liquid form of methyl dibromoglutarate. Consequently no conclusion can be drawn from these condensations as to the configuration of the dibromoglutaric acids corresponding to these esters.

Moreover it was found that the liquid methyl dibromoglutarate was readily transformed into the solid isomeride by sodium methoxide in methyl-alcoholic solution. This transformation is analogous to that which occurs with the $\alpha\alpha'$-dibromo- and $\alpha\alpha'$-di-iodo-adipic esters (compare Part II, J., 1924, **125**, 1945). The transformation did not appear to be quantitative, but as methyl dibromoglutarate reacts very readily with sodium methoxide with loss of hydrogen bromide even at low temperatures, it was difficult to be certain on this point. The liquid modification of methyl di-iodoglutarate was also largely transformed by sodium methoxide in methyl-alcoholic solution into the solid isomeride; but part of the di-iodo-ester was converted into the iodo*cyclo*propane ester, which on hydrolysis gave 1-*iodo*cyclo*propane*-1 : 2-*dicarboxylic acid*, m. p. 175—176°.

Of the two forms of methyl *cyclo*butanetetracarboxylate, it is probable that the liquid form corresponds to the *meso*-configuration (a) and the solid to the racemic configuration (b) (p. 2391). The two esters were separately hydrolysed under identical conditions. The *cyclo*butanetricarboxylic acid obtained from the solid ester

melted at 171—172° and is therefore identical with the acid termed *trans* by Goldsworthy and Perkin (*loc. cit.*). The acid obtained from the liquid ester melted at 144—145° and is consequently identical with the acid named *cis* by these authors. It seems probable that the high-melting acid has the *trans* or racemic configuration (e) and that the low-melting acid has one of the *cis*- or *meso*-configurations (c and d).

An attempt was made to settle the configuration of the acid, m. p. 171—172°, by resolution into optical enantiomorphs, but unexpected difficulty was encountered. After six recrystallisations of the brucine salt of this acid, only a very slightly dextrorotatory acid was obtained. A second attempt with quinine as the active base was more successful, an acid of $[\alpha]_D^{18°}$ 31·34° being obtained, but the pure *d-cyclo*butanetricarboxylic acid has not yet been isolated. Sufficient evidence, however, has been obtained to indicate that the high-melting acid has the *dl*-configuration (e). It is hoped to investigate further the configurations of the *cyclo*-butanetricarboxylic acids.

Experimental.

The αα′-Dibromoglutaric Esters.—The methyl and ethyl esters of the αα′-dibromoglutaric acids were prepared from glutaric acid by Ingold's method (J., 1921, **119**, 316), mixtures of the *meso*- and *dl*-isomerides being obtained. Ethyl αα′-dibromoglutarate distilled at 162°/14 mm. (Found: Br, 46·4. Calc., Br, 46·2%), and the methyl ester at 150°/14 mm. (Found: Br, 50·2. Calc., Br, 50·3%).

The methyl ester of the *meso*-dibromoglutaric acid, m. p. 170°, was obtained by boiling the pure acid in methyl alcohol containing 10% of its weight of sulphuric acid. After being distilled under reduced pressure, this ester solidified and was recrystallised from methyl alcohol. *Methyl* meso-*αα′-dibromoglutarate* so obtained melts at 45° (Found: Br, 50·5. $C_7H_{10}O_4Br_2$ requires Br, 50·3%).

The methyl ester of the *dl*-dibromoglutaric acid, m. p. 142°, obtained in a similar manner was an oil, b. p. 143—145°/10 mm.

The αα′-Di-iodoglutaric Esters.—Methyl dibromoglutarate was heated in methyl-alcoholic solution with sodium iodide, and the product poured into ice-water. The semi-solid mass so obtained was filtered and the solid recrystallised three times from methyl alcohol. *Methyl αα′-di-iodoglutarate* crystallises in prisms, m. p. 75° (Found: I, 61·8. $C_7H_{10}O_4I_2$ requires I, 61·6%).

The oil left after filtering off the solid ester was extracted with ether, the ether solution washed with sodium thiosulphate solution to remove free iodine, then with water and finally dried with sodium sulphate. After evaporation of the ether a pale yellow oil was

left which showed no sign of crystallisation at — 20° (Found: I, 61·9%). This liquid *methyl di-iodoglutarate* gradually turns brown owing to the liberation of free iodine and is slowly transformed into the stable solid isomeride. It cannot be distilled without extensive decomposition.

Action of Sodium Methoxide on the Dibromo- and Di-iodo-glutaric Esters.—Liquid methyl dibromoglutarate (7 g.), dissolved in methyl alcohol (10 c.c.), was treated with a solution of sodium (0·25 g.) in methyl alcohol (10 c.c.); after 10 minutes, 5 g. of the solid ester had crystallised. With a larger proportion of sodium methoxide, sodium bromide is precipitated and methyl bromo*cyclo*propane-dicarboxylate formed.

Liquid methyl di-iodoglutarate was treated in a similar manner. A small proportion of the solid isomeride crystallised, but the di-iodo-ester reacted readily with sodium methoxide with the formation of an iodo*cyclo*propane ester and sodium iodide even at — 20°.

At the ordinary temperature methyl di-iodoglutarate is rapidly converted by sodium methoxide into methyl iodo*cyclo*propane-dicarboxylate, which on hydrolysis with hydrochloric acid yields 1-*iodo*cyclo*propane*-1 : 2-*dicarboxylic acid.* This acid is readily soluble in water but can be recrystallised from hydrochloric acid; it melts at 176—177° (Found: C, 23·6; H, 1·9; I, 49·8. $C_5H_5O_4I$ requires C, 23·4; H, 1·9; I, 49·6%).

Condensation of the αα′-Dibromoglutaric Esters with Sodiomalonic Ester.—Sodium (5 g.) was dissolved in alcohol (80 c.c.), treated with ethyl malonate (36 g.), the whole cooled in ice, and ethyl dibromoglutarate (38 g.) added slowly. After standing for an hour, the mixture was boiled on the steam-bath for an hour. The product was poured into water, the oil extracted with ether and, after evaporation of the ether, fractionated under 12 mm. The following fractions were obtained: (1) below 110°; (2) 110—170°; (3) 190—200°. Fraction (1) consisted of unchanged ethyl malonate; fraction (2) was hydrolysed with hydrochloric acid, and the acid obtained recrystallised from acetone–benzene. It was identified as 1-bromo*cyclo*propane-1 : 2-dicarboxylic acid, m. p. 175° (Ingold, *loc. cit.*) (Found: C, 28·6; H, 2·4; Br, 38·2. Calc., C, 28·7; H, 2·4; Br, 38·2%); when treated with aniline in ether, it gave a characteristic salt, m. p. 132°. Fraction (3) was redistilled and obtained as an oil, b. p. 195—198°/12 mm., which proved to be *ethyl* cyclo*butane*-1 : 2 : 2 : 3-*tetracarboxylate* (V) (Found: C, 56·0; H, 7·1. $C_{16}H_{24}O_8$ requires C, 55·8; H, 7·0%); the yield was about 50% of the original dibromoglutaric ester.

The aqueous solution obtained after extracting the oil with

ether was acidified, the red oil formed extracted with ether, and the ether solution washed with water and dried with calcium chloride. The oil left after evaporation of the ether could not be distilled without decomposition, but after remaining in a vacuum over sulphuric acid for some time it had the composition $C_{14}H_{15}O_7$ (Found: C, 55·7; H, 6·2. Calc., C, 56·4; H, 6·0%). It is considered to be a bridged-ring ester of constitution (VI). A thick red oil of identical composition and character was obtained by the following condensation: sodium (2·5 g.) was dissolved in alcohol (50 c.c.), treated with ethyl malonate (18 g.) and with ethyl bromo-*cyclo*propanedicarboxylate (29 g.), the mixture boiled on the steam-bath for an hour and then poured into water. No *cyclo*propane-malonic ester was found, but on acidifying the aqueous solution the bridged-ring ester was precipitated.

In order to discover whether one or two *cyclo*butane esters were formed in the condensation of dibromoglutaric ester with malonic ester the condensation was repeated with the methyl esters. The reaction product was separated into unchanged methyl malonate, methyl bromo*cyclo*propanedicarboxylate, and methyl *cyclo*butane-tetracarboxylate, which distilled at 193—195°/15 mm. and partly solidified in a freezing mixture. The semi-solid mass was pressed on porous plate, and the dry solid so obtained recrystallised from aqueous methyl alcohol. Solid *methyl* cyclo*butane*-1 : 2 : 2 : 3-*tetracarboxylate* crystallised in needles, m. p. 78° (Found: C, 50·0; H, 5·6. $C_{12}H_{16}O_8$ requires C, 50·0; H, 5·6%). The oil was extracted from the porous plate with ether and, after evaporation of the ether, distilled. Liquid *methyl* cyclo*butane*-1 : 2 : 2 : 3-*tetracarboxylate* distilled at 193—195°/15 mm. and showed no sign of crystallisation at — 20° (Found: C, 50·2; H, 5·5%). The total yield of methyl *cyclo*butane ester was about 30%.

This condensation was also performed in dry benzene solution. Sodium (5 g.) was finely powdered under benzene, treated with methyl malonate (29 g.), and the whole heated on the steam-bath until the sodium had disappeared. Methyl dibromoglutarate (34 g.) was added, and the mixture boiled for 2 hours. The product was washed with water, the benzene distilled off, and the residual oil fractionated, a 70—80% yield of *cyclo*butane ester being thus obtained.

The pure *meso*- and *dl*-isomerides of methyl dibromoglutarate were separately condensed in benzene solution with methyl malonate and in both cases a mixture of the solid and liquid forms of methyl *cyclo*butanetetracarboxylate was obtained.

Synthesis of the Bridged-ring Sodium Derivative (VIII).—Methyl dibromoglutarate was treated in methyl alcohol with sodium

methoxide, the product poured into water, the oil extracted with ether, and the crude ester fractionated, *methyl* 1-*bromo*cyclo*propane*-1 : 2-*dicarboxylate* distilling at 134—135°/15 mm. (Found: Br, 33·5. $C_7H_9O_4Br$ requires Br, 33·7%).

Sodium (6·5 g.) was dissolved in methyl alcohol (80 c.c.), mixed with methyl malonate (19 g.) and methyl bromo*cyclo*propanedicarboxylate (33 g.), and the whole boiled on the steam-bath for 6 hours. The yellow solid formed was filtered off, stirred with a little water to remove sodium bromide, and again filtered. The *sodium* derivative was recrystallised from methyl alcohol, in which it was sparingly soluble (Found: Na, 8·0. $C_{11}H_{11}O_7Na$ requires Na, 8·3%).

The aqueous solution of the sodium derivative was acidified, and the precipitated solid purified by solution in ammonia and reprecipitation. It was recrystallised from chloroform–carbon tetrachloride and finally from aqueous methyl alcohol. The substance melted at 200° and is provisionally represented by formula (VIII) (Found: C, 51·5; H, 5·0. $C_{11}H_{12}O_7$ requires C, 51·5; H, 4·7%).

Condensation of the αα′-Dibromoglutaric Esters with Sodiocyanoacetic Ester.—Sodium (5 g.) was dissolved in alcohol, treated with ethyl cyanoacetate (25 g.), and to the cold mixture ethyl dibromoglutarate (38 g.) was added. The mixture was boiled on the steam-bath for 2 hours, poured into water, and the oil extracted with ether. No oil was formed on acidifying the aqueous solution. After evaporation of the ether, the residual oil was distilled under 20 mm. and the following fractions were obtained: (1) below 120°, mainly ethyl cyanoacetate; (2) 120—190°, a few drops only; (3) 190—220°. Fraction (3) was redistilled and 23 g. of *ethyl* 2-*cyano*cyclo*butane*-1 : 2 : 3-*tricarboxylate* (IX), b. p. 210—215°/20 mm., were obtained (Found: N, 4·3. $C_{14}H_{19}O_6N$ requires N, 4·7%).

The cyano-ester was hydrolysed by cold alcoholic potash to the *tripotassium* salt of an amide-acid (Found: K, 34·5. $C_8H_6O_7NK_3$ requires K, 34·0%). Hydrolysis with hydrochloric acid yielded *cyclo*butanetricarboxylic acid.

The pure solid and liquid forms of methyl dibromoglutarate were separately condensed with methyl sodiocyanoacetate, and in both cases a mixture of a solid and a liquid form of methyl cyano*cyclo*butanetricarboxylate was obtained, the total yield being about 60% of the theoretical. Solid *methyl* 2-*cyano*cyclo*butane*-1 : 2 : 3-*tricarboxylate* crystallises from ether in prisms, m. p. 111—112° (Found: N, 5·5. $C_{11}H_{13}O_6N$ requires N, 5·5%). The liquid isomeride distils at 185—190°/12 mm. (Found: N, 5·8%). The proportion

of solid to liquid isomeride formed from the solid methyl dibromoglutarate was 1 : 2, and from the liquid dibromo-ester 1 : 3.

Condensation of Ethyl αα′-Dibromoglutarate with Ethyl Sodiobenzoylacetate.—Sodium (5 g.) was dissolved in alcohol, treated with ethyl benzoylacetate (41 g.), the mixture cooled in ice, and ethyl dibromoglutarate (37 g.) added. The reaction mixture was boiled on the steam-bath for 6 hours, the product poured into water, the oil extracted with ether and, after evaporation of the ether, fractionated. The following fractions were obtained: (1) below 150°, 10 g.; this consisted almost entirely of ethyl bromo*cyclo*propanedicarboxylate (yield about 40% of the dibromo-ester used). (2) 150—220°; this consisted of unchanged ethyl benzoylacetate. (3) 230—240°, 12 g.; this proved to be *ethyl* 2-*benzoyl*cyclo*butane*-1 : 2 : 3-*tricarboxylate* (Found: C, 64·4; H, 6·4. $C_{20}H_{24}O_7$ requires C, 63·8; H, 6·4%); yield about 30% of the original dibromo-ester.

The ester was hydrolysed by boiling with alcoholic potash. Water was added, the alcohol evaporated, the solution acidified, and the oily solid so formed extracted with ether, which removed benzoic acid (m. p. 121°). The aqueous solution was evaporated to dryness with hydrochloric acid, and the residue extracted with ether in a Soxhlet apparatus. The ether was evaporated, the residual syrup taken up with water, the solution filtered and left in a vacuum over sulphuric acid; *cis-cyclo*butanetricarboxylic acid, m. p. 143°, slowly crystallised.

Condensation of Ethyl αα′-Dibromoglutarate with Ethyl Sodioacetoacetate.—This condensation was performed in an exactly similar manner to that described above. The main products of the reaction were ethyl bromo*cyclo*propanedicarboxylate (40% of theoretical) and *ethyl* 2-*acetyl*cyclo*butane*-1 : 2 : 3-*tricarboxylate* (30% of theoretical), b. p. 195°/18 mm. (Found: C, 56·8; H, 7·1. $C_{15}H_{22}O_7$ requires C, 57·3; H, 7·0%). The ester was hydrolysed in the usual way with alcoholic potash and *cis-cyclo*butanetricarboxylic acid, m. p. 143°, was obtained.

The cyclo*Butane*-1 : 2 : 3-*tricarboxylic Acids.*—When ethyl *cyclo*butanetetracarboxylate was hydrolysed by boiling with hydrochloric acid, a mixture of two *cyclo*butanetricarboxylic acids was obtained, which was difficult to separate into its components. The mixture, which began to melt at 135° but was not completely molten until 160°, contained *cis-cyclo*butane-1 : 2 : 3-tricarboxylic acid, m. p. 143°, and *trans-cyclo*butane-1 : 2 : 3-tricarboxylic acid, m. p. 172° (Goldsworthy and Perkin, J., 1914, **105**, 2665).

The solid and liquid forms of methyl *cyclo*butanetetracarboxylate were separately hydrolysed in an identical manner. Each ester

was kept with methyl-alcoholic potash for several days, water was then added, and the alcohol evaporated. The solution was neutralised with dilute nitric acid, and the lead salt precipitated with lead nitrate. The lead salt suspended in water was decomposed with hydrogen sulphide, and the filtered solution evaporated. In each case a clear syrup was obtained which showed no sign of crystallisation. It was heated at 150° until no more carbon dioxide was evolved; the residue was dissolved in hot water and left in a desiccator to crystallise. The acid obtained from the solid ester solidified completely and was recrystallised from hydrochloric acid; it melted at 171—172° and was therefore *trans-cyclo*butane-1 : 2 : 3-tricarboxylic acid (Found : C, 44·5; H, 4·3. Calc., C, 44·7; H, 4·2%).

The acid obtained from the liquid *cyclo*butane ester deposited first a small amount of the *trans*-acid, but the residual syrup eventually solidified and after recrystallisation from hydrochloric acid melted at 144—145°. It was therefore *cis-cyclo*butane-1 : 2 : 3-tricarboxylic acid (Found : C, 44·5; H, 4·1%).

Resolution of trans-cyclo*Butane*-1 : 2 : 3-*tricarboxylic Acid.*—The tricarboxylic acid (15 g.) was dissolved in hot water (360 c.c.), mixed with brucine (113 g.), the whole heated on the steam-bath, the excess of brucine filtered off, and the filtrate allowed to cool. The brucine salt which separated was recrystallised a number of times from water; the rotation was observed each time in a 2-dcm. tube, the amount of substance taken being made up to 20 c.c. with methyl alcohol.

	1	2	3	4	5	6
G. of salt	0·2406	0·1120	0·1308	0·1150	0·1034	0·1232
α obs.	−1·16°	−0·41°	−0·47°	−0·41°	−0·37°	−0·44°
$[\alpha]_D^{18°}$	−38·3°	−36·6°	−35·9°	−35·6°	−35·8°	−36·1°

The rotations of the different fractions did not seem to approach a constant value. The last fraction was therefore decomposed with ammonia, and the filtrate from the precipitated brucine evaporated to dryness with a slight excess of hydrochloric acid. The residue was extracted with cold acetone; after evaporation of the acetone, a solid acid, m. p. 165—170°, was obtained which was only slightly dextrorotatory (0·1070 g. made up to 20 c.c. with water gave $\alpha = +0{\cdot}04°$ in a 2-dcm. tube at 18°; whence $[\alpha]_D^{18°} = +3{\cdot}7°$).

In a second attempt, the acid (1 mol.) was mixed with quinine (2 mols.) dissolved in alcohol; after standing for an hour, the salt which had separated was collected and decomposed with ammonia. The acid so obtained was then treated in a similar manner. The salt formed had the composition $C_7H_8O_6,2C_{20}H_{24}O_2N_2,C_2H_6O$

(Found: C, 66·9; H, 6·9; N, 6·3. $C_{49}H_{62}O_{10}N_4$ requires C, 66·7; H, 7·0; N, 6·3%). After three operations, an acid was obtained, m. p. 155—160°, of which 0·1340 g. made up to 20 c.c. with water gave $\alpha = +0{\cdot}42°$; whence $[\alpha]_D^{18°} = +31{\cdot}34°$. Owing to the small amount of acid available, it was not possible to proceed further with the resolution, but sufficient evidence has been obtained that the *trans-cyclo*butanetricarboxylic acid, m. p. 172°, has the *dl*-configuration.

One of us (H. R. I.) wishes gratefully to acknowledge the receipt of a grant from the Chemical Society Research Fund which has defrayed a part of the cost of this investigation.

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CCCXXVI.—*The Catalysis by Alumina of the Reaction between Ethyl Alcohol and Ammonia.*

By GORDON WILLIAM DORRELL.

PREVIOUS work on this reaction has been mainly qualitative (Sabatier and Mailhe, *Compt. rend.*, 1909, **148**, 898; 1910, **150**, 823; 1911, **153**, 160, 1204), but some quantitative results have been given by Smolenski (*Roczniki Chem.*, 1921, **1**, 232). In a paper published after the present work was finished, Brown and Reid (*J. Physical Chem.*, 1924, **28**, 1067) state that specially prepared silica gel is the most efficient catalyst for converting aliphatic alcohols into amines; they give no results for the conversion with alumina as catalyst.

The object of this research was to study the effect of varying such factors as temperature, time of contact, and the ratio of alcohol to ammonia. Throughout, the catalyst was to be the same; and alumina was finally chosen in preference to other well-known aminating catalysts, *e.g.*, thoria, because it has scarcely any dehydrogenating action upon alcohol.

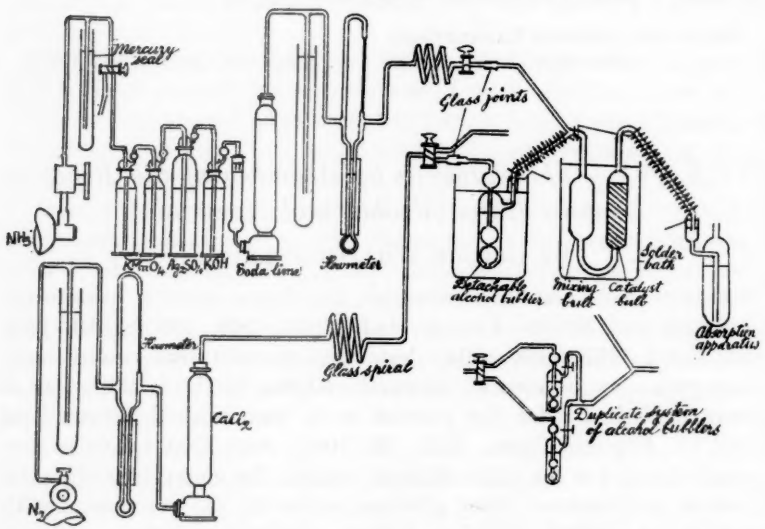
Theoretical treatment by the Nernst equation shows that the reaction: $C_2H_5{\cdot}OH + NH_3 = C_2H_5{\cdot}NH_2 + H_2O$ (where the formation of secondary and tertiary amines is ignored) is exothermic to the extent of 5920 calories, and that the amount of conversion in the system in equilibrium, although greater at low temperatures than at high, does not vary rapidly with temperature.

Apparatus and Method.—Ammonia from a cylinder (Fig. 1) was passed through two ammoniacal solutions of potassium permangan-

ate, a solution of silver sulphate, and one of caustic potash. It was then dried by soda-lime, and its rate of flow measured.

Nitrogen * from a cylinder was passed through a second flow-meter, dried by calcium chloride, and allowed to bubble through absolute ethyl alcohol (dried by potassium carbonate and distilled), immersed in a thermostat. The quantity of alcohol evaporated was determined by its temperature and by the rate of flow of the nitrogen. By electrical heating, the emerging nitrogen–alcohol mixture was kept at a temperature sufficiently high to prevent condensation of the alcohol in the connecting tubes.

FIG. 1.



The ammonia, nitrogen, and alcohol were allowed to mix and were preheated in a bulb filled with pieces of glass tube, before entering a second bulb containing the catalyst. Both bulbs were immersed in the same bath of solder, and the temperature of the catalyst was taken as that registered by a mercury thermometer (calibrated against standard thermometers) the bulb of which was situated between the preheater and the catalyst bulb.

The smaller diagram shows a modified form of the apparatus used in the later part of the work. By means of a second bubbler containing alcohol it was possible to avoid interruption in the flow of alcohol and ammonia over the catalyst while the products of the preceding experiment were being removed for analysis. In

* No difference was detected in the results of those experiments where the nitrogen had been passed over heated copper gauze.

addition, the preliminary sweeping through the apparatus with ammonia and the final washing out with nitrogen which had to be done in the first part of the work were eliminated, and a much simpler technique was evolved.

The Catalyst.—Only one sample of alumina was used, which is referred to as Al_2O_3-1. It was prepared by adding excess of ammonia, *d* 0·880, to a strong solution of aluminium nitrate, washing the precipitate, and drying it in stages at 100°, 160°, and 400°, after which it was broken into fragments about 4 mm. in diameter; these were filled into the bulb so that the catalyst, which weighed about 25 g., occupied a volume of 50 c.c.

Analysis.—The amount of alcohol used was determined by weighing the bubbler before and after the experiment. A sufficiently approximate value of the quantity of nitrogen was obtained from flowmeter–time observations. The quantity of ammonia passed (correct to 1—6%, depending upon the rate of flow of the gas) was determined directly from flowmeter–time observations; for very small gas velocities, *e.g.*, 3 c.c. per minute, this value was subject to the larger error. A more accurate value could be obtained from a knowledge of the amount of basic nitrogen absorbed in standard acid (see below); since no ammonia decomposes into nitrogen and hydrogen, and a negligible quantity of non-basic substances is produced, under the given conditions, from the decomposition of amines, the quantity of ammonia used must be equivalent to the amount of basic nitrogen absorbed in acid.

No separate analysis of each of the primary, secondary, and tertiary amines produced was made, but the three were estimated together, as "amines" or "ammonia converted," by Weber and Wilson's method (*J. Biol. Chem.*, 1918, **35**, 385), in which the solution of amines and ammonia is treated with yellow mercuric oxide, whereby ammonia is quantitatively removed. The amines were distilled from the alkaline filtrate from the mercuric oxide into standard acid, the excess of which was then estimated. The results obtained from several blank analyses with the most satisfactory mercuric oxide indicated that the probable error in the final conversion value was 0·5%.

Expression of the Results.—The percentage conversion of ammonia into amines,* $\%E$, is given by the expression Mols. of amines absorbed $\times$ 100/mols. of ammonia used. The symbol $\%E_0$ denotes the percentage conversion in the particular case where the molecular ratio of ammonia to alcohol is unity; it is calculated from the equation $\%E_0 = \%E/R$, where R = mols. of alcohol used/mols.

* No figures for the amount of conversion of alcohol into amines have been given.

of ammonia used. For example, in a series of experiments it was desired to keep the molecular ratio of alcohol to ammonia equal to 1·0; but experimentally this is difficult. Actually the ratio varied between 0·7 and 1·2. However, by dividing such a diverging molecular ratio into the corresponding $\%E$, the true value of the latter for a molecular ratio of unity is obtained. The results given later (Fig. 3) show that the correction just discussed is valid when the molecular ratio of alcohol to ammonia lies between 0·6 and 1·2.

Effect of Temperature.—The effect of varying the temperature on the amount of ammonia converted is shown in Table I.

TABLE I.

Ratio $C_2H_5{\cdot}OH : NH_3 = 1{\cdot}0$.
Mean rate of flow of $NH_3 = 9{\cdot}2$ c.c. (at *N.T.P.*) per min.
Mean rate of flow of $N_2 = 50$ c.c. (at *N.T.P.*) per min.

Temp. of catalyst bath.	No. of expts.	$\%E_0$. Mean.
344°	9	11·5
293	4	15·3
239	3	9·3

Since the quantity of ammonia (or alcohol) passing over the catalyst in a given time is the same for all three temperatures, its time of contact with the catalytic surface at 344° is different from that at 239°; actually, the times of contact of 1 mol. of ammonia at 239° and 344°, respectively, are in the ratio 1·2 : 1. A correction for this factor, if it were possible to apply it, would not affect the values of $\%E_0$ to any serious extent.

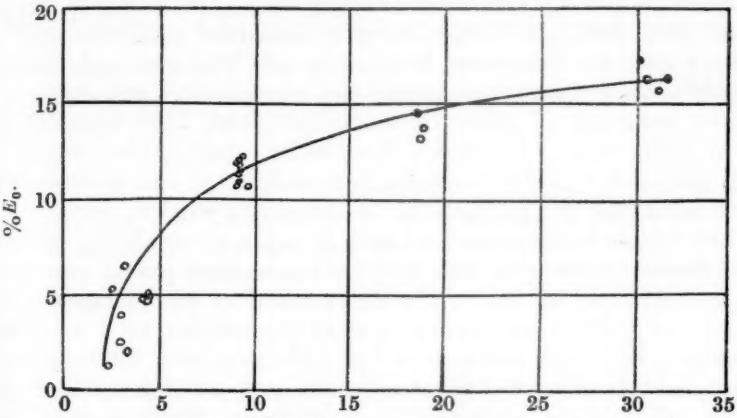
The important result of this table is that the optimum temperature of the reaction under the given conditions is about 300°.

Effect of Rate of Flow of the Reacting Gases.—The curve in Fig. 2 illustrates the results obtained in experiments at 344° in which the molecular ratio of alcohol to ammonia was 1·0 and the speed of the ammonia varied from 2 to 32 c.c. (*N.T.P.*) per minute. The rates of flow of the alcohol vapour and nitrogen were varied so that the partial pressure of the latter was always 5·6 times that of the former (or of the ammonia). The finer particles of the catalyst were carried away by the gases when the speed of the ammonia exceeded 32 c.c. per minute, and therefore the curve could not be followed experimentally up to its maximum.

Contrary to the usual experience that increased time of contact means increased amount of reaction product owing to the state of equilibrium being approached, this curve shows that the conversion of the ammonia falls off rapidly when the speed of the reacting gases diminishes, especially when the speed of the ammonia is less than 5 c.c. per minute. It will be shown later that the most probable cause of this is the decomposition of the amine itself.

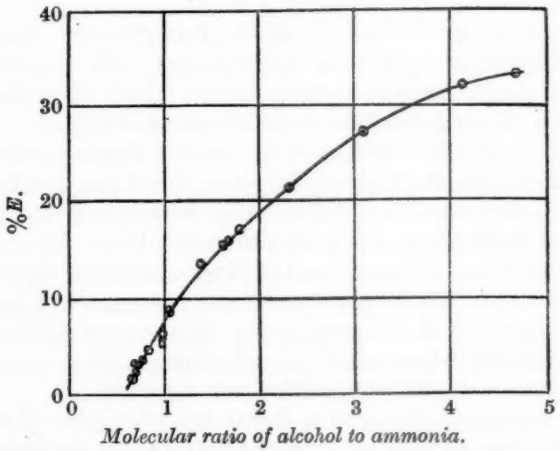
Effect of Varying Relative Quantities of Alcohol and Ammonia.—The curve in Fig. 3, plotted from the results of experiments at 344° in which the speeds of the ammonia and nitrogen were 9·4 and

FIG. 2.



50 c.c. per minute, respectively, shows the relation between $\%E$ and the molecular ratio $C_2H_5{\cdot}OH : NH_3$. It is practically linear where this ratio lies between 0·6 and 1·2; but its slope decreases

FIG. 3.



as the ratio increases, from which it is evident that the effect of using excess of alcohol is the production of larger quantities of secondary and tertiary amines, because the amount of ammonia converted per mol. of alcohol is proportionately small at large

molecular ratios, owing to one mol. of ammonia tending to react with more than one of alcohol.

The increase in activity of the catalyst indicated by the curve will be discussed later.

Decomposition of Ethylamine.—Sabatier and Gaudion (*Compt. rend.*, 1917, **165**, 222, 310), working with a nickel catalyst at 300°, were unable to decompose ethylamine into hydrogen and acetonitrile because it broke down so readily into ammonia and ethylene. Upson and Sands (*J. Amer. Chem. Soc.*, 1922, **44**, 2306) found that its decomposition, in presence of a kaolin catalyst, into ethylene and ammonia is favoured by low temperature; it can be assumed that below 500° the products are ammonia and ethylene only.

Ethylamine * was evaporated from an aqueous solution by means of a stream of nitrogen, and the mixed gases were passed over the Al_2O_3-1 catalyst at 344°. The mean speed of the nitrogen was 7 c.c. (at *N.T.P.*) per minute, and of the ethylamine 3 c.c. per minute (calc.); the duration of the experiment was 130 minutes. The products were led through standard acid, and the unabsorbed gases collected, by aspiration, over mercury. The quantities of ammonia and amines in the acid were estimated and allowance was made for the amount of ammonia present in the original ethylamine. The unabsorbed gases were analysed for ethylene. The percentage decompositions of the ethylamine calculated from the quantities of ammonia and ethylene produced were respectively 60 and 33.

These two values should be equal if ethylamine decomposes thus: $C_2H_5{\cdot}NH_2 = C_2H_4 + NH_3$. However, the smaller result alone is sufficiently large to account for the falling off in the values of $\%E_0$ when the speeds of the gases are small (Fig. 2).

Action of the Alumina Catalyst on Ammonia.—Certain irregularities were observed in the first two experiments (Nos. 1 and 2 in Table III) in connexion with the amount of ammonia passing over the catalyst; as measured by titration of the absorbing acid, there was apparently a loss of ammonia. The explanation first conceived, that some of the ammonia was being decomposed into nitrogen and hydrogen, was finally disposed of by carrying out a special gas analysis of the products obtained when ammonia and nitrogen alone were passed over the catalyst; no decomposition was detected.

The loss was finally found to be due to the adsorption of ammonia by the fresh alumina catalyst. In Table II are the results obtained with a second catalyst, which consisted of 13·5 g. of fresh alumina

* As the ethylamine contained a small quantity of ammonia, for which an approximate correction was made, the result can be regarded as qualitative only.

prepared in a similar way to Al_2O_3-1. This was kept at 344°, and nitrogen and ammonia were led over it at definite rates. The emerging gases were passed for a definite time (t) through standard acid; and the amount of ammonia present (v') was determined by back titration. The quantity of ammonia (v) entering the catalyst chamber during the same time was determined from flowmeter time observations. The amount of ammonia adsorbed by the alumina is the difference $v - v'$. The absorption acid was changed after each time interval (col. 1).

TABLE II.

Speed of NH_3 = 9—10 c.c. (at *N.T.P.*) per min. (equiv. to 246·3 c.c. of *N*/10-acid per hour). Speed of N_2 = 50 c.c. (at *N.T.P.*) per min.
t = time in mins. from start of flow of NH_3 over Al_2O_3. v and v' are expressed as c.c. of *N*/10-acid.

t.	v.	v'.	$v - v'$.
5	20·5	0·1	20·4
15	61·6	9·5	52·1
35	143·7	78·3	65·4
55	225·7	146·9	78·8
105	431·0	340·5	90·5

If a curve is drawn, the figures of column 4 being plotted against those of column 1, it will be seen that the adsorption of the ammonia is approaching its maximum value after a period of 105 minutes.

The Catalyst Al_2O_3-1.—After the preceding experiment had been made, the original catalyst was examined. Its colour had changed from white to buff; and some fragments were black throughout, showing that the reacting gases must have penetrated right into the granules.

Catalytic poisoning was entirely absent, for the mean $\%E_0$ of experiments 3—6 is 11·4 and of experiments 19—23, 11·6 (Table III).

The increase in activity of the catalyst referred to in connexion with the curve (Fig. 3) does not affect the general results to any serious extent. Immediately before this particular series of experiments was made, the catalyst had been (1) accidentally shaken, (2) thoroughly saturated with ethylamine vapour during the work on the decomposition of this substance. It is quite possible that its activity would change as a result of such treatment. Pease and Yung (*J. Amer. Chem. Soc.*, 1924, **46**, 390) found that alumina which had been used in the catalytic decomposition of ether appeared to be activated with respect to alcohol, and the yield of ethylene was nearly doubled.

Experimental Results in Detail.—In Table III are the more important data appertaining to the experiments; these were carried out in the order given.

TABLE III.

No. of expt.	Temp. of catalyst.	Speed of NH_3 in c.c./min. (*N.T.P.*).	Speed of N_2 in c.c./min. (*N.T.P.*).	Duration of expt. in mins.	Ratio of alcohol to ammonia.	% *E*.	% E_0.
1	344°	5·0	50	31·5	1·60	2	—
2	,,	8·5	,,	32	0·89	5·8	—
3	,,	9·4	,,	60	0·76	9·4	12·3
4	,,	9·1	,,	40	1·06	11·3	10·7
5	,,	9·6	,,	50	0·91	9·7	10·7
6	,,	9·2	,,	70	0·94	11·4	12·1
7	293	9·0	50	45	0·99	15·3	15·5
8	,,	9·4	,,	50	0·95	16·3	17·1
9	,,	8·8	,,	40	1·14	14·4	12·6
10	,,	9·0	,,	,,	1·06	16·6	15·7
11	239	5·7	50	40	1·33	12·4	9·3
12	,,	9·0	,,	50	0·94	8·4	9·0
13	,,	9·2	,,	60	0·95	9·0	9·5
14	344	3·3	17	60	0·57	1·2	2·1
15	,,	2·4	,,	45	0·58	3·1	5·3
16	,,	2·3	20	60	0·97	1·2	1·3
17	,,	2·9	,,	,,	0·65	1·7	2·6
18	,,	3·0	,,	70	0·70	2·8	4·0
19	,,	9·2	50	40	0·92	9·9	10·8
20	,,	9·1	,,	,,	0·87	9·9	11·3
21	,,	9·2	,,	,,	0·87	10·1	11·7
22	,,	9·2	,,	,,	0·85	10·3	12·1
23	,,	9·2	,,	,,	1·13	13·4	11·9
24	344	18·7	100	30	0·93	12·3	13·2
25	,,	18·8	,,	,,	0·93	12·6	13·6
26	,,	18·6	,,	,,	0·93	13·5	14·5
27	344	4·2	25	40	0·74	3·6	4·9
28	,,	4·4	,,	60	0·73	3·7	5·1
29	,,	4·5	,,	,,	0·70	3·4	4·9
30	,,	4·5	,,	,,	0·75	3·7	4·9
31	344	3·0	20	330	0·87	5·8	6·7
32	344	30·7	160	30	0·87	14·2	16·3
33	,,	31·7	,,	,,	0·90	14·7	16·3
34	,,	31·2	,,	,,	0·94	14·7	15·6
35	,,	30·2	,,	,,	1·00	17·6	17·6
36	345	9·7	48	50	1·61	25·6	
37	344	9·8	,,	60	1·38	23·5	
38	,,	10·0	50	50	0·97	16·2	
39	,,	9·3	,,	45	1·06	18·6	
40	,,	9·6	,,	,,	1·02	19·0	
41	,,	9·3	48	60	0·82	14·7	
42	343	9·4	,,	50	0·70	13·2	
43	,,	9·6	50	60	0·96	15·2	
44	,,	9·4	,,	,,	0·68	12·3	
45	344	9·1	,,	40	0·96	15·4	
46	,,	9·7	,,	,,	0·75	13·6	
47	,,	9·7	,,	30	0·67	13·2	
48	,,	9·6	,,	60	0·64	11·7	
49	343	9·3	,,	30	2·30	31·3	
50	344	9·3	,,	40	1·79	27·1	
51	,,	9·3	,,	,,	1·64	25·7	
52	,,	9·0	,,	30	3·10	37·1	
53	,,	9·2	,,	,,	4·69	43·1	
54	,,	9·0	,,	,,	4·13	42·2	

Summary.

The catalysis by alumina of the reaction between alcohol and ammonia has been studied from the point of view of the quantity of ammonia converted into amine.

The effects of varying (*a*) the temperature, (*b*) the speed of the reacting gases, (*c*) the ratio of alcohol to ammonia have been determined.

The decomposition of ethylamine itself has been found to occur under the conditions obtaining in the main reaction; ammonia is not decomposed to any measurable extent by the catalyst.

Alumina adsorbs ammonia readily, and a table is given showing the relation between the amount of ammonia adsorbed and the time of flow of the ammonia over the catalyst.

No sign of catalytic poisoning could be detected.

The author desires to express his thanks to Professor F. G. Donnan, who suggested the investigation; and to the Advisory Council of the Department of Scientific and Industrial Research for a maintenance grant during the period of the research.

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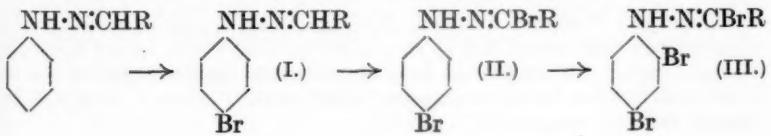
LONDON. [*Received, June 23rd,* 1925.]

CCCXXVII.—*Substituted* iso*Diazomethanes.*

By FREDERICK DANIEL CHATTAWAY and ARTHUR JOHN WALKER.

WHEN bromine (1 mol.) is allowed to act upon *o*-nitrobenzaldehydephenylhydrazone (1 mol.), the first product easily isolated is *o*-nitrobenzaldehyde-*p*-bromophenylhydrazone (I). The further action of bromine yields first an orange-red *dibromo*-derivative and finally a yellow *tribromo*-derivative, m. p. 110°. These compounds can also be formed by the bromination of the *p*-bromo- and 2 : 4-dibromophenylhydrazones of *o*-nitrobenzaldehyde, but they differ entirely in properties from the isomeric nuclear-substituted hydrazones. Since on oxidation they yield *o*-nitrobenzoic acid, they must be ω-bromo-derivatives, strictly analogous with those obtained from *m*- and *p*-nitrobenzaldehydephenylhydrazones (this vol., p. 1687; see also p. 975), substitution following the course (R = *o*-$C_6H_4{\cdot}NO_2$)



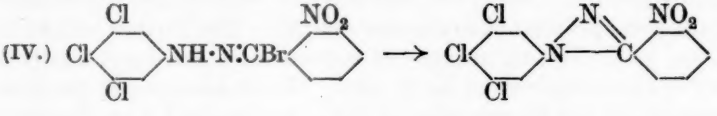
The final product, *ω-bromo-o-nitrobenzaldehyde-2 : 4-dibromophenylhydrazone* (III), can be recrystallised without change from chloroform, benzene, or acetic acid, but on warming for a short time with alcohol it loses hydrogen bromide, forming a compound * which explodes with great violence when heated.

This also occurs when the ω-bromo-derivative is warmed in acetic acid with sodium acetate, but elimination of hydrogen bromide is most readily effected by shaking a solution of the ω-bromo-derivative in benzene with a little aqueous ammonia, or a small quantity of pyridine.

The action of bromine upon *o*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone yields a *trichloromonobromo*-derivative (m. p. 115°) which similarly may be made to lose hydrogen bromide and form an explosive compound containing all the original chlorine, but no bromine. The formation of the explosive compound does not therefore take place by the elimination of the nuclear, but of the ω-halogen. The occupation of both *o*-positions and the *p*-position by chlorine in this compound excludes the possibility of it being formed by the elimination of the ω-halogen with an *o*- or the *p*-hydrogen of the phenylhydrazine nucleus.

In a similar way, the formation of an explosive derivative from *ω-bromo-o-nitrobenzaldehyde-3 : 4 : 5-trichlorophenylhydrazone* (IV), in which both the *m*-positions are occupied, excludes the possibility of an elimination of hydrogen bromide between the ω-bromine and the hydrogen in the *m*-position.

The most probable explanation of the reaction is that the ω-halogen is eliminated with the imino-hydrogen of the hydrazone, forming an unstable, three-atom *iso*diazomethane ring, thus:



If the bromination of *o*-nitrobenzaldehydephenylhydrazone be carried out in the presence of sodium acetate, the formation of ω-bromo-*o*-nitrobenzaldehyde-*p*-bromophenylhydrazone and the elimination of hydrogen bromide from this take place successively, yielding the explosive 1-p-*bromophenyl*-3-o-*nitrophenyl*isodiazomethane (VI) as the product of the one operation:

* Ciusa and Vecchiotti (*Gazzetta*, 1916, **46**, i, 240) appear to have had this compound in their hands, but as they failed to observe the loss of hydrogen bromide during recrystallisation from alcohol, they assumed that it was an ω-bromo-derivative, having a structure which we have shown to be that of the entirely different compound, m. p. 110°.

$$C_6H_5\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot NO_2 \longrightarrow C_6H_4Br\cdot NH\cdot N{:}CBr\cdot C_6H_4\cdot NO_2 \longrightarrow$$

$$C_6H_4Br\cdot N\!\!<\!\!\begin{matrix}N\\ \|\\ C\end{matrix}\!\!\cdot C_6H_4\cdot NO_2 \quad \text{(VI.)}$$

An excess of bromine has no action on this final explosive product under the conditions of the experiment, as might be expected, there being no hydrogen attached to the nitrogen united with the aryl residue, replacement of which by halogen appears to be a necessary preliminary to the intramolecular rearrangement by which it passes into the nucleus.

Other ω-bromo-*o*-nitrobenzaldehydehydrazones yield similar explosive compounds, which also must therefore be regarded as *iso*diazomethanes, *e.g.*,

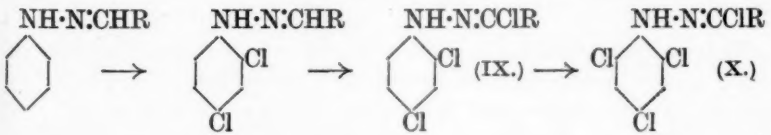
(VII.) $(2:4\text{-})C_6H_3Br_2\cdot N\!\!<\!\!\begin{matrix}N\\ \|\\ C\end{matrix}\!\!\cdot C_6H_4\cdot NO_2$ and

$(2:4:6\text{-})C_6H_2Cl_3\cdot N\!\!<\!\!\begin{matrix}N\\ \|\\ C\end{matrix}\!\!\cdot C_6H_4\cdot NO_2$ (VIII.)

The action of chlorine upon *o*-nitrobenzaldehydephenylhydrazone is similar to the action of bromine, although naturally more energetic. The first product easily isolated is *o*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone. The further action of chlorine upon this yields a trichloro-derivative (m. p. 132°) which must be *ω-chloro-o-nitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazone*,

$$C_6H_3Cl_2\cdot NH\cdot N{:}CCl\cdot C_6H_4\cdot NO_2 \text{ (IX)},$$

since it differs in its properties from *o*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone and yields *o*-nitrobenzoic acid on oxidation. The final product of the chlorination is a tetrachloro-derivative, which, since it can also be obtained by the chlorination of *o*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone, must be *ω-chloro-o-nitrobenzaldehyde*-2 : 4 : 6-*trichlorophenylhydrazone* (X). The course of the reaction may therefore be represented thus (R = *o*-$C_6H_4\cdot NO_2$) :



Like the ω-bromo-*o*-nitrobenzaldehydephenylhydrazones, the ω-chloro-*o*-nitrobenzaldehydephenylhydrazones lose hydrogen halide when their benzene solutions are warmed with pyridine or ammonia, forming highly explosive compounds containing similar three-atom, *iso*diazomethane rings, *e.g.*, (X) ⟶ (VIII).

EXPERIMENTAL.

The Bromination Products of o-*Nitrobenzaldehydephenylhydrazone, and their* iso*Diazomethane Derivatives.*

To a suspension of 5 g. (1 mol.) of *o*-nitrobenzaldehydephenylhydrazone in 25 c.c. of acetic acid was added a solution of 3 g. (1 mol.) of bromine in the same solvent. An orange solution was formed, from which red crystals of *o*-nitrobenzaldehyde-*p*-bromophenylhydrazone separated, m. p. 183° after recrystallisation from alcohol.

ω-*Bromo*-o-*nitrobenzaldehyde*-p-*bromophenylhydrazone* (II).—The addition of more bromine (6 g.; 2 mols.) to a similar quantity of *o*-nitrobenzaldehydephenylhydrazone yielded an orange solution from which, on pouring into water, a viscid, red solid was precipitated. This was dissolved in a little warm ether and cooled, when a small quantity of red crystals of *o*-nitrobenzaldehyde-2 : 4-dibromophenylhydrazone separated, m. p. 204° after recrystallisation from alcohol.

The ethereal mother-liquor yielded on evaporation an amorphous red solid. This lost hydrogen bromide so readily that it could not be recrystallised, but it was shown to consist of ω-bromo-*o*-nitrobenzaldehyde-*p*-bromophenylhydrazone by conversion into its crystalline *iso*diazomethane derivative (below), a yield of over 3·5 g. (90% of the theoretical) being obtained from 5 g. of the red solid.

1-p-*Bromophenyl*-3-o-*nitrophenyl*iso*diazomethane* (VI).—A solution of 5 g. of ω-bromo-*o*-nitrobenzaldehyde-*p*-bromophenylhydrazone in 20 c.c. of warm benzene was shaken with 5 c.c. of concentrated aqueous ammonia. The mixture set to a mass of yellow crystals, which were collected, and recrystallised from chloroform, in which the compound is moderately soluble, and from which it separates in yellow needles; these explode at 144° without melting * (Found: Br, 24·7; N, 12·9. $C_{13}H_8O_2N_3Br$ requires Br, 25·1; N, 13·2%).

This *iso*diazomethane is most conveniently prepared by adding to 5 g. of *o*-nitrobenzaldehydephenylhydrazone and 10 g. of anhydrous sodium acetate suspended in acetic acid, a solution of 6 g. of bromine (2 mols.) in acetic acid; the hydrazone dissolves and fine, yellow crystals of the *iso*diazomethane separate (yield 5 g. after washing with water and recrystallisation from chloroform).

* The explosion point does not vary by more than a degree with the rate of heating. It was found that the determination of a mixed explosion point (analogous with a mixed melting point) could be employed to establish the identity of these compounds, the explosion point of a mixture being generally below the explosion point of either of the pure constituents.

The same compound is obtained by the action of bromine (1 mol.) upon *o*-nitrobenzaldehyde-*p*-bromophenylhydrazone under similar conditions.

ω-Bromo-o-nitrobenzaldehyde-2 : 4-dibromophenylhydrazone (III).—To a cooled suspension of 5 g. (1 mol.) of *o*-nitrobenzaldehydephenylhydrazone in 25 c.c. of acetic acid was added a solution of 10 g. of bromine (3 mols.) in acetic acid. A yellow solution was formed which deposited compact crystals of the ω-bromo-derivative. This crystallises from acetic acid, in which it is easily soluble, in compact, pale yellow needles, m. p. 110° (yield 7 g. or 70%). It is sparingly soluble in ligroin and easily soluble in chloroform or benzene (Found : Br, 50·4. $C_{13}H_8O_2N_3Br_3$ requires Br, 50·2%).

The same compound (m. p. 110°) was similarly prepared by adding bromine (1 mol.) to a suspension of *o*-nitrobenzaldehyde-2 : 4-dibromophenylhydrazone in acetic acid.

A small quantity of the substance, when boiled for 3 hours with an alkaline solution of potassium permanganate, yielded *o*-nitrobenzoic acid, m. p. 144°, thus showing that no halogen had entered the aldehyde nucleus.

1-2 : 4 - *Dibromophenyl* - 3 - o - *nitrophenyl*isodiazomethane (VII).—ω-Bromo-*o*-nitrobenzaldehyde-2 : 4-dibromophenylhydrazone (5 g.), dissolved in 25 c.c. of warm benzene, was shaken with 5 c.c. of concentrated aqueous ammonia. The mixture became hot and set to a mass of yellow crystals. These were recrystallised from chloroform, in which the compound was sparingly soluble, and from which it separated in long, yellow needles which exploded violently at 145—146° without melting (yield almost theoretical) (Found : Br, 40·5 ; *M*, ebullioscopic in chloroform, 373. $C_{13}H_7O_2N_3Br_2$ requires Br, 40·3% ; *M*, 397).

The compound can be obtained from ω-bromo-*o*-nitrobenzaldehyde-2 : 4-dibromophenylhydrazone in several other ways. For example, it separates when dry ammonia gas is passed into a solution of the ω-bromo-derivative in benzene, or when a small quantity of pyridine is added. It is also formed when a solution of the ω-bromo-compound in acetic acid is warmed gently with sodium acetate, and when a solution of the same compound in alcohol is gently boiled for a few minutes.

ω-Bromo-o-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone,

$$C_6H_3Cl_2{\cdot}NH{\cdot}N{:}CBr{\cdot}C_6H_4{\cdot}NO_2.$$

—A solution of 2·5 g. of bromine (1 mol.) in acetic acid was added to a suspension of 5 g. of *o*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone (1 mol.) in 50 c.c. of warm acetic acid. The yellow solution formed deposited, on cooling, crystals of the *ω-bromo*-derivative in clusters of pale yellow needles, m. p. 122°. It is

moderately easily soluble in acetic acid and easily soluble in benzene (Found : Cl + Br, 38·6. $C_{13}H_8O_2N_3Cl_2Br$ requires Cl + Br, 38·8%).

1-2 : 4-*Dichlorophenyl*-3-o-*nitrophenyl*isodiazomethane (corresponding to VII) separated almost instantaneously when a benzene solution of ω-bromo-*o*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone was shaken with concentrated aqueous ammonia. It crystallises from chloroform, in which it is easily soluble, in bright yellow, six-sided, slender prisms which explode at 140° (Found : Cl, 23·2. $C_{13}H_7O_2N_3Cl_2$ requires Cl, 23·05%).

ω-Bromo-o-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone, $C_6H_2Cl_3{\cdot}NH{\cdot}N{:}CBr{\cdot}C_6H_4{\cdot}NO_2$, separated when a solution of 2·5 g. of bromine (1 mol.) was added to 5 g. of *o*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone in 50 c.c. of acetic acid. It was recrystallised from acetic acid, in which it is moderately easily soluble. It is also easily soluble in chloroform or benzene.

It exists in two polymorphic modifications, and when a solution in acetic acid is cooled separates first in light yellow needles, which in the warm solvent transform rapidly into pale yellow, compact prisms, m. p. 115—116° (Found : Cl + Br, 43·9. $C_{13}H_7O_2N_3Cl_3Br$ requires Cl + Br, 44·0%).

1-2 : 4 : 6-*Trichlorophenyl*-3-o-*nitrophenyl*isodiazomethane (VIII) separated when a solution of ω-bromo-*o*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone in benzene was shaken with concentrated aqueous ammonia. It dissolves easily in chloroform or benzene and sparingly in ligroin. It crystallises from chloroform–ligroin in bright yellow, long prisms, which explode at 163° (Found : Cl, 31·1; *M*, ebullioscopic in chloroform, 365. $C_{13}H_6O_2N_3Cl_3$ requires Cl, 31·1%; *M*, 343·5).

ω-Bromo-o-nitrobenzaldehyde-3 : 4 : 5-trichlorophenylhydrazone (IV) separated when 2·5 g. of bromine (1 mol.) were added to 5 g. (1 mol.) of *o*-nitrobenzaldehyde-3 : 4 : 5-trichlorophenylhydrazone suspended in 250 c.c. of warm acetic acid. It was recrystallised from this solvent, in which it is moderately easily soluble, and from which it separates in pale yellow needles, m. p. 170° (decomp.) (Found : Cl + Br, 43·8. $C_{13}H_7O_2N_3Cl_3Br$ requires Cl + Br, 44·0%).

1-3 : 4 : 5-*Trichlorophenyl*-3-o-*nitrophenyl*isodiazomethane (V) separated when a solution of ω-bromo-*o*-nitrobenzaldehyde-3 : 4 : 5-trichlorophenylhydrazone in benzene was shaken with concentrated aqueous ammonia. It is sparingly soluble in benzene, chloroform, or acetic acid, and separates from these solvents in compact, yellow plates, which explode at 151° (Found : Cl, 31·2. $C_{13}H_6O_2N_3Cl_3$ requires Cl, 31·1%).

1-p-*Chlorophenyl*-3-o-*nitrophenyl*isodiazomethane was prepared from *o*-nitrobenzaldehyde-*p*-chlorophenylhydrazone, without the

isolation of an intermediate ω-bromo-derivative. It separated as a yellow, crystalline mass when a solution of bromine (1 mol.) was added to a suspension of the hydrazone (1 mol.) and an excess (2 mols.) of sodium acetate in acetic acid. It crystallises from this solvent, in which it is moderately easily soluble, in bright yellow needles, which explode at 147° (Found: Cl, 12·9. $C_{13}H_8O_2N_3Cl$ requires Cl, 13·0%).

Action of Chlorine upon o-*Nitrobenzaldehydephenylhydrazone.*—Chlorination proceeds more cleanly in chloroform than in acetic acid. Its progress is accompanied by marked changes in the colour of the solution, which serve as a convenient guide when it is desired to arrest the process at some intermediate point.

A slow current of chlorine was passed into a cooled suspension of 5 g. of *o*-nitrobenzaldehydephenylhydrazone in 50 c.c. of chloroform, until the solid had dissolved to form a red solution. This on standing yielded dark red crystals, which after recrystallisation from alcohol melted at 192°, and proved to be *o*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone.

ω-*Chloro*-o-*nitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazone* (IX).—In a second experiment the stream of chlorine was continued until the solution became dark brown. From this solution, on addition of an equal volume of cold alcohol, ω-*chloro*-o-*nitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazone* separated. It crystallises from chloroform, in which it is moderately easily soluble, in compact, yellow prisms, m. p. 132° (Found: Cl, 31·0. $C_{13}H_8O_2N_3Cl_3$ requires Cl, 30·9%).

The same compound is more readily prepared by passing chlorine into a suspension of *o*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone in chloroform until the solid just dissolves, and then adding an equal volume of alcohol, when it separates in a fairly pure state.

A small quantity of the substance, when boiled for some time with an alkaline solution of potassium permanganate, yielded *o*-nitrobenzoic acid, m. p. 144°.

ω-Chloro-*o*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone, like the ω-bromo-compound, loses hydrogen halide when pyridine is added to its benzene solution or when it is shaken with ammonia. The product, 1-2 : 4-dichlorophenyl-3-*o*-nitrophenyl*iso*diazomethane (expl: 140°), is the same in both cases and has already been described.

ω-*Chloro*-o-*nitrobenzaldehyde*-2 : 4 : 6-*trichlorophenylhydrazone* (X).—In a third experiment the passage of chlorine into the suspension in chloroform of *o*-nitrobenzaldehydephenylhydrazone was continued until no more was absorbed, and the colour of the solution had changed to a light brown. The excess of chlorine was evaporated off, and an equal volume of cold alcohol added, when ω-*chloro*-o-

nitrobenzaldehyde-2 : 4 : 6-*trichlorophenylhydrazone* separated as a yellow, crystalline solid. Yield from 5 g. of the original hydrazone, 4·5 g. It dissolves easily in chloroform or benzene, but is sparingly soluble in ligroin. It crystallises from benzene–ligroin in fine, yellow needles, m. p. 107° (Found: Cl, 37·5. $C_{13}H_7O_2N_3Cl_4$ requires Cl, 37·5%).

A small quantity when boiled for 3 hours with alkaline potassium permanganate solution yielded *o*-nitrobenzoic acid, m. p. 144°.

The same compound was prepared in a similar manner by the action of chlorine upon *o*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone.

ω-Chloro-*o*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone when dissolved in benzene and shaken with aqueous ammonia was converted into 1-2 : 4 : 6-trichlorophenyl-3-*o*-nitrophenyl*iso*diazomethane, which separated from the solution in almost theoretical quantity. This exploded at 163° and was identical with the compound similarly obtained from ω-bromo-*o*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone (p. 2412).

The ω-halogeno-*o*-nitrobenzaldehydephenylhydrazones described here all yield deep green colorations when a trace of an oxidising agent (nitric acid or ferric chloride) is added to their solutions in strong sulphuric acid. The *iso*diazomethane derivatives dissolve in sulphuric acid, giving yellow solutions which are unaffected by the addition of oxidising agents.

Both the ω-halogeno-*o*-nitrobenzaldehydephenylhydrazones and their *iso*diazomethane derivatives are decomposed by alcoholic potash, yielding as one of the products a halogen-substituted benzene, *e.g.*, 1-2 : 4 : 6-trichlorophenyl-3-*o*-nitrophenyl*iso*diazomethane yields 1 : 3 : 5-trichlorobenzene. A similar decomposition is effected by ammonia in *alcoholic* solution. The course of these reactions is at present under investigation.

THE QUEEN'S COLLEGE, OXFORD. [*Received, July 17th*, 1925.]

CCCXXVIII.—*The Isomerism of the Oximes. Part XXIII. Acyl Derivatives.*

By OSCAR L. BRADY and GERALD PATRICK MCHUGH.

IN this series of papers a considerable amount of work has been published on the various acyl derivatives of the aldoximes (see particularly J., 1913, **103**, 1613; 1916, **109**, 650; 1923, **123**, 1190, 2163; 1924, **125**, 1087; this vol., p. 844), and the object of the present communication is to fill in certain gaps and to summarise the position.

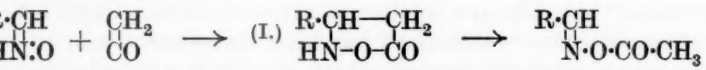
The action of benzoyl chloride on the α-aldoximes * has been studied by Minunni and his co-workers (*Gazzetta*, 1892, **22**, ii, **166**; 1896, **26**, i, 456) and by Forster and Judd (J., 1910, **97**, 256). The former prepared the benzoyl derivatives from the α-aldoximes by treatment with benzoyl choride in ethereal solution, the latter tried to prepare the isomeric benzoyl derivatives from β-benzaldoxime and *p*-triazo-β-benzaldoxime by avoiding the presence of hydrogen chloride, which would be likely to cause inversion (compare the acetyl-β-aldoximes). They were, however, unsuccessful, both isomerides yielding the same benzoyl derivative. The action of benzoyl chloride on a solution in excess of sodium hydroxide of a number of other α-aldoximes has been investigated and in every case a benzoyl derivative was obtained, which, on hydrolysis with alkali, regenerated the original oxime. It had previously been found that benzoyl chloride converts the otherwise stable β-cinnamaldoxime and *o*-methoxy-β-cinnamaldoxime into α-benzoyl derivatives from which the α-oximes could be obtained by alkaline hydrolysis (Brady and Thomas, J., 1922, **121**, 2104; Brady and Grayson, J., 1924, **125**, 1419). This reaction is apparently a general one and it has been found that benzoylation by the Schotten-Baumann method converts β-benzaldoxime, *o*-, *m*-, and *p*-nitro-, *p*-methoxy-, and 3 : 4-methylenedioxy-β-benzaldoximes into the corresponding α-benzoyl derivatives. Similar results were obtained by benzoylating in pyridine solution with benzoylpyridinium chloride in spite of all precautions to avoid isomeric change. These results are somewhat remarkable, since ethyl chloroformate with an alkaline solution of the β-aldoximes invariably gave the nitrile, and acetylpyridinium chloride with a pyridine solution of the β-aldoximes also gave the nitrile.

The action of keten on the aldoximes promised to be of interest, since the behaviour of phenylcarbimide in giving inversion of configuration (Brady and Dunn, J., 1916, **109**, 650) suggested that keten, also an additive reagent, might act upon the α-aldoxime to give the acetyl-β-oxime. This expectation was, however, not realised, the α-aldoximes giving acetyl-α-aldoximes. With β-aldoximes and keten, the acetyl compound could not be isolated in a pure state, but treatment of the crude product with sodium hydroxide gave the corresponding nitrile, indicating the presence of the acetyl-β-aldoxime. The acetyl-β-aldoximes are very sensitive to traces of

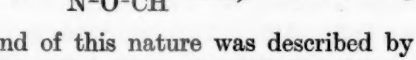
* α-Aldoximes are those which on treatment with acetic anhydride and sodium carbonate give acetyl derivatives which regenerate the oxime on alkaline hydrolysis; β-aldoximes, those which give the nitrile under these conditions; α-acyl derivatives, those which on alkaline hydrolysis give the α-aldoxime; and β-acyl derivatives, those which give the nitrile (compare Brady and Bishop, this vol., p. 1357).

acid, being thereby converted into the acetyl-α-aldoxime, and it was possible that in the first case traces of hydrogen bromide were carried over by the keten; if, however, this had been the case, one would have expected a similar result when the β-aldoximes were employed, whereas here there was no doubt that the acetyl-β-aldoxime was formed.

If keten added to the C:N and N:O double bonds in the tautomeric form of the oximes, RCH:NH:O, in a manner similar to that suggested for phenylcarbimide (J., 1916, **109**, 659), an aryl*iso*oxazolidone (I) would be formed:



This might be expected to tautomerise to the acetylaldoxime, or to split off acetic acid and give the nitrile in a similar manner to the γ-alkyl*iso*oxazoles (II) (Claisen, *Ber.*, 1903, **36**, 3672).



A compound of this nature was described by Posner (*Annalen*, 1912, **389**, 97), who obtained γγ-diphenyl*iso*oxazolidone (III) by the action of hydroxylamine on β-phenylcinnamic ester; this compound might be formed by the action of keten on the tautomeric form of diphenylketoxime, and since, according to Posner, the compound was comparatively stable, there should have been no difficulty in isolating it; however, only acetyldiphenylketoxime was obtained in the reaction.

The acetyl-β-aldoximes have been described by Hantzsch (*Ber.*, 1891, **24**, 38; *Z. physikal. Chem.*, 1894, **13**, 509), who gives three general methods for their preparation, but, with the exception of acetyl-β-benzaldoxime, no experimental details for the individual compounds. His methods have been tried with four β-aldoximes, but our products differ considerably from his and could not be obtained free from unchanged oxime. Hantzsch publishes no analyses of the compounds other than acetyl-β-benzaldoxime and we are not convinced that other acetyl-β-aldoximes have, as yet, been obtained in the pure state.

In connexion with the inversion of configuration brought about by phenylcarbimide, the action of phenylcarbamyl chloride on the sodium salts of the α-aldoximes has been investigated; here the carbanilino-derivative of the α-oxime was obtained, there being no indication of the formation of the corresponding β-derivative.

Table I summarises the principal results which have been obtained in this series of investigations, but it is a matter of some difficulty to interpret them; α indicates that the acyl derivative formed in the reaction, on hydrolysis with sodium hydroxide, regenerates the α-aldoxime; β, that the acyl derivative, on alkaline hydrolysis, gives the nitrile; N indicates that the nitrile is formed; A, the aldehyde.

TABLE I.

Oxime.	Acetic anhydride.	Benzoyl chloride.	Diphenylcarbamyl chloride.	Diethylcarbamyl chloride.	Phenylethylcarbamyl chloride.	Ethyl chloroformate.	2:4-Dinitrochlorobenzene.	2:4:6-Trinitrochlorobenzene.	Phenylcarbimide.	α-Naphthylcarbimide.
Benzaldoxime	α	α	α	β	—	α	α	β	β	α + β	α
,,	β	β	α	β	—	—	N	A	A + N	β	β
o-Nitrobenzaldoxime	α	α	α	β	—	—	β	β	β	α*	—
,,	β	β	α	β	—	—	N	A	A + N	β	—
m-Nitrobenzaldoxime	α	α	α	β	α	α	α	β	β	α + β	α
,,	β	β	α	β	—	—	N	A	A + N	β	β
p-Nitrobenzaldoxime	α	α	α	β	β	β	β	β	β	α + β	α
,,	β	β	α	β	β	β	N	A	A + N	β	β
p-Methoxybenzaldoxime	α	α	α	β	—	—	β	β	β	α + β	α
p-Methoxybenzaldoxime	β	β	α	—	—	—	N	A	A + N	β	β
3 : 4-Methylenedioxybenzaldoxime	α	α	α	—	—	α	β	β	β	α + β	α
3 : 4-Methylenedioxybenzaldoxime	β	β	α	—	—	—	N	A	A + N	β	β
Cinnamaldoxime	α	α	α	—	—	—	α	β	β	α*	α
,,	β	β	α	—	—	—	N	A	A + N	β	β
o-Methoxybenzaldoxime	α	α	α	β	—	—	α	β	β	α*	α
p-Dimethylaminobenzaldoxime	α	α	α	β	—	—	α	β	β	β	α

* In these cases the carbanilino-compound separated very slowly and isomeric change of any β-isomeride formed may have occurred.

It will be noticed that *o*-methoxybenzaldoxime and *p*-dimethylaminobenzaldoxime, which are known only in the α-form, give, in certain cases, derivatives which apparently have the β-configuration. The main problems, however, that have to be considered are: (1) How far it is justifiable to assume that all acyl derivatives which on alkaline hydrolysis give the nitrile have a similar configuration? (2) If the above assumption is correct, why one reagent, *e.g.*, ethyl chloroformate, brings about inversion of some oximes but not of others, whereas another similar reagent, diphenylcarbamyl chloride, always brings about inversion, and a third, benzoyl chloride, never. (3) Why phenylcarbimide causes inversion, but α-naphthylcarbimide does not do so. (4) Why benzoyl chloride is unique in yielding, with aqueous sodium hydroxide solutions of the β-aldoximes,

the benzoyl derivatives of the α-oxime rather than that of the β-oxime or the nitrile. (5) The nature of the very unstable, yellow carbanilino- and α-naphthylcarbamyl compounds which are frequently the first products of the action of the carbimides on the β-aldoximes (Goldschmidt and van Rietschoten, *Ber.*, 1893, **26**, 2087; Brady and Thomas, J., 1922, **121**, 2105; see also experimental part).

In connexion with the first point, adopting the new configuration of the aldoximes (Brady and Bishop, *loc. cit.*), the stereoisomeric acyl derivatives may be represented:

(IV.) $\begin{matrix} R\cdot CH \\ \| \\ N\cdot O\cdot COR' \end{matrix}$ Acyl derivative of α-oxime.

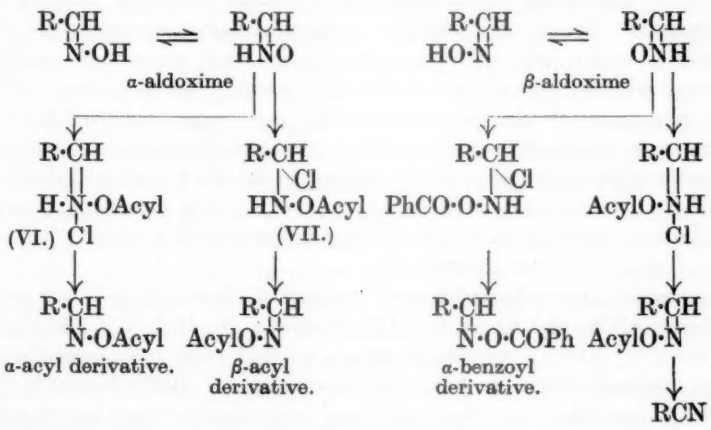
$\begin{matrix} R\cdot CH \\ \| \\ R'CO\cdot O\cdot N \end{matrix}$ (V.) Acyl derivative of β-oxime.

In normal cases, on alkaline hydrolysis, *trans*-elimination of acid will occur, (IV) regenerating the oxime and (V) giving the nitrile, but it is conceivable that in special cases *cis*-elimination of acid might readily take place and (IV) here give the nitrile. Consequently it might be argued that the carbethoxy-compounds obtained from *p*-methoxy-, 3 : 4-methylenedioxy-, *o*- and *p*-nitro-α-benzaldoximes have the same configuration (IV) as these oximes but that here *cis*-elimination of the acid readily occurs. Against this view, however, are the facts, first, the same carbethoxy-compounds were obtained from the β-aldoximes and secondly, the carbethoxy-compound obtained from *p*-nitro-α-benzaldoxime on boiling with alcohol gave a second carbethoxy-derivative, which behaved in a normal manner on hydrolysis, regenerating the original α-aldoxime; on the above hypothesis, this would indicate a change from configuration (IV) to configuration (V) and a reversal on hydrolysis. The first change is unlikely in view of the well-established reverse tendency, whilst if the latter contingency be admitted, the whole problem of oxime configuration would be thrown into indescribable confusion.

Another possibility is that in certain cases *N*-acyl derivatives are formed on the analogy of the *N*-ethers and that the carbethoxy-compounds prepared from *p*-methoxy-, 3 : 4-methylenedioxy-, *o*- and *p*-nitro-α-benzaldoximes, which on hydrolysis give the nitrile, should be represented as $R\cdot CH{:}N(:O)\cdot CO_2Et$, the effect of heating the carbethoxy-compound from *p*-nitro-α-benzaldoxime being the transference of the carbethoxy-group from N to O; against this, however, must be placed the nature of the absorption spectrum of *N*-derivatives, which does not accord with that of these carbethoxy-compounds. Moreover, one would then have to regard as *N*-acyl derivatives the diethylcarbamyl and phenylethylcarbamyl com-

pounds obtained from *p*-nitro-α-benzaldoxime, differentiating these from the diphenylcarbamyl derivatives; if the latter class are included, the dinitrophenyl- and trinitrophenyl-compounds, prepared from the α-aldoximes, would have to follow, but the action of 2 : 4-dinitrochlorobenzene and picryl chloride on the β-aldoximes is quite abnormal, the only explanation that appears possible being that it is in this case that an *N*-substituted compound is formed which is too unstable to be capable of free existence (Brady and Truszkowski, J., 1924, **125**, 1087; Brady and Klein, this vol., p. 844). In addition, the *N*-methyl ethers of the aldoximes are readily hydrolysed by alkali, not to the nitrile, but to the aldehyde. The idea that all acyl derivatives which give nitriles on hydrolysis are *N*-substituted compounds cuts at the very basis of the Hantzsch-Werner hypothesis and is difficult to maintain for other reasons, some of which have been given in previous papers. There seems, therefore, every reason to suppose that all acyl derivatives which on hydrolysis give the nitrile have the same configuration.

The application of the octet theory, although it suggested the very complicated nature of the electron changes which probably occur during acylation, did not elucidate the problem and after a careful consideration of many possible hypotheses, including an ionisation theory, we are still unable to advance any view that fits the facts better than that suggested by Dunn and one of us (J., 1916, **109**, 650). The new configuration being adopted, and the aldoximes being regarded as tautomeric, the acyl halide can add on in two ways, either at the N:O double bond (VI) or at both the C:N and N:O double bonds (VII); removal of hydrogen chloride produces no change in configuration in the first case, but does so in the second; similarly, in the case of the β-aldoxime :



With the α-aldoximes, the method of addition is governed partly by the nature of the aryl group R, *e.g.*, in the case of the carbethoxy-compounds, and partly by the nature of the acyl halide, *e.g.*, diphenylcarbamyl chloride; with the β-aldoximes, it seems to be decided solely by the nature of the acyl chloride, benzoyl chloride being the only one, so far investigated, which adds on at both double bonds.

The arguments previously adduced for the formation of the carbanilino-compounds must still hold in general, but it seems more probable that the yellow compounds obtained by the action of arylcarbimides on β-oximes are formed by the addition of the carbimide at first to the C:N double bond only, (VIII) then undergoing tautomeric change, the group migrating to the O, giving (IX).

$$\begin{array}{l} \mathrm{R{\cdot}CH} \\ \mathrm{ONH} \end{array} \longrightarrow \text{(VIII.)} \begin{array}{l} \mathrm{R{\cdot}CH{-}NR} \\ \mathrm{O{:}NH{-}C{:}O} \end{array} \longrightarrow \begin{array}{r} \mathrm{R{\cdot}CH} \\ \mathrm{RNH{\cdot}CO_2{\cdot}N} \end{array} \text{(IX.)}$$

The nitrone structure here suggested, as in the case of the *N*-ethers, would account for the colour (compare also Staudinger and Miescher, *Helv. Chim. Acta*, 1919, **2**, 554, for the addition of diphenylketen to ketoximes).

EXPERIMENTAL.

Action of Benzoyl Chloride on α-Aldoximes.—The α-aldoxime (3 g.) was dissolved in 2*N*-sodium hydroxide (100 c.c.), benzoyl chloride (3 g.) added, and the mixture well shaken and cooled; when the odour of the chloride had disappeared, the solid was collected, washed, and crystallised. The orientation of the product was determined in each case by hydrolysis with warm 2*N*-sodium hydroxide, when a clear solution was obtained and no ammonia evolved, indicating the absence of a nitrile produced from a β-derivative. From the solution carbon dioxide precipitated the α-oxime, which was identified by the method of mixed melting points, whilst hydrochloric acid subsequently gave benzoic acid. No indication of the presence of the acid corresponding to the oxime was obtained. Benzoyl-*o*-nitro-α-benzaldoxime, as is usually the case with derivatives of this oxime, underwent profound decomposition on warming with alkali, but when left in contact with 2*N*-sodium hydroxide at room temperature until a clear solution was obtained, it reacted normally.

Benzoyl-o-nitro-α-benzaldoxime separated from alcohol in pale greenish-white plates, m. p. 112° (Found: N, 10·2. $C_{14}H_{10}O_4N_2$ requires N, 10·3%), *benzoyl-p-nitro-α-benzaldoxime* from acetone in pale greenish-white, rectangular plates, m. p. 196° (Found: N, 10·4%), *benzoyl-3 : 4-methylenedioxy-α-benzaldoxime* from acetic acid

in white plates, m. p. 168° (Found : N, 5·3. $C_{14}H_{10}O_4N$ requires N, 5·2%), *benzoyl-o-methoxy-α-benzaldoxime* from alcohol in white plates, m. p. 96° (Found : N, 5·6. $C_{15}H_{13}O_3N$ requires N, 5·5%), and *benzoyl-p-dimethylamino-α-benzaldoxime* from acetone and water in greenish-white plates, m. p. 138° (Found : N, 10·3. $C_{16}H_{16}O_2N_2$ requires N, 10·4%).

In addition, the benzoyl derivatives of α-benzaldoxime, *m*-nitro-, and *p*-methoxy-α-benzaldoximes (Minunni and Corselli, *Gazzetta*, 1892, **22**, 164) were prepared in an analogous manner from the corresponding α-aldoximes, and their configuration determined by hydrolysing them to the α-aldoximes with 2*N*-sodium hydroxide.

Action of Benzoyl Chloride on β-Aldoximes.—β-Benzaldoxime, *o*-, *m*-, and *p*-nitro-, *p*-methoxy-, and 3 : 4-methylenedioxy-β-benzaldoximes were benzoylated in a similar manner to the α-derivatives. In each case the corresponding benzoyl-α-aldoxime was obtained, which was identified by a mixed melting point and by hydrolysis to the α-oxime. The benzoyl chloride was shaken with a little sodium hydroxide immediately before use, in case any acid in it should bring about conversion. The benzoylation was carried out at 0° and the products were washed with iced water. They were crystallised by dissolution in cold acetone and precipitation by the cautious addition of water in order to avoid isomeric change, which might be brought about by the use of hot solvents, but no indication of the formation of a β-isomeride was obtained. In another series of experiments β-benzaldoxime, *m*-nitro-, and 3 : 4-methylenedioxy-β-benzaldoxime were dissolved in dry pyridine and cooled to 0° ; a solution of the calculated amount of benzoyl chloride in dry pyridine at 0° was added, and the mixture kept at 0°. The product was poured on to crushed ice and extracted with ether, the extract washed, dried over sodium sulphate, and the ether evaporated at room temperature. In every case the benzoyl-α-aldoxime was obtained. Similar results were obtained at −23° (compare Forster and Judd, *loc. cit.*). Acetylation of β-aldoximes under similar conditions gives the nitrile, but no indication of the formation of this compound was obtained during the benzoylation. 3 : 4-Methylenedioxy-β-benzaldoxime (5 g.) was dissolved in dry ether, sodium (0·7 g.) dissolved in a minimum of alcohol added, the precipitated sodium salt collected, washed with dry ether, rapidly dried on a porous tile, suspended in dry ether, and the calculated amount of benzoyl chloride added. After 2 hours, the solution was filtered, and on evaporating the ether at room temperature benzoyl-3 : 4-methylenedioxy-α-benzaldoxime was obtained.

Action of Keten on α-Aldoximes.—The keten was prepared (Staudinger and Klever, *Ber.*, 1908, **41**, 594) by the action of zinc

filings on 50 g. of bromoacetyl bromide in 250 c.c. of dry ether in a current of hydrogen. Ether and keten distilled over and were passed directly into a dry ethereal solution of 1 g. of the oxime; this was then evaporated over solid sodium hydroxide in a continuously evacuated desiccator and the solid residue pressed on a tile. 3 : 4-Methylenedioxy-α-benzaldoxime gave a crude product which melted alone at 98—104°, at 102—104° when mixed with acetyl-3 : 4-methylenedioxy-α-benzaldoxime, and at 105° after one crystallisation from benzene. This was identified as the α-acetyl derivative by comparison with a specimen prepared by the action of acetic anhydride at 30° on 3 : 4-methylenedioxy-α-benzaldoxime followed by treatment with sodium carbonate solution. *Acetyl-3 : 4-methylenedioxy-α-benzaldoxime* crystallised from alcohol in fine, white needles, m. p. 105° (Found: N, 6·9. $C_{10}H_9O_4N$ requires N, 6·7%).

In the cases of *m*- and *p*-nitro-α-benzaldoximes the reaction was incomplete even after 24 hours, although the solution had still a strong odour of keten. Accordingly the ether was evaporated, and the crude product washed with a small amount of cold 2*N*-sodium hydroxide, which removed unchanged oxime, identified as the α-isomeride after precipitation with carbon dioxide. The residues, after drying on a tile, melted at 121° (*m*-compound; when mixed with acetyl-*m*-nitro-α-benzaldoxime, at 126°) and 124—129° (*p*-compound); in each case the pure acetylnitro-α-benzaldoxime was obtained after one crystallisation from alcohol.

In all three cases the crude product, on hydrolysis with warm 2*N*-sodium hydroxide, gave the corresponding α-oxime, no nitrile or acid being detected. This result and the melting points of the crude products indicate that no appreciable amount of acetyl-β-aldoxime had been formed and subsequently converted into the α-isomeride during crystallisation; for the former is immediately converted by cold sodium hydroxide into the nitrile and subsequently into the carboxylic acid.

Action of Keten on β-Aldoximes.—3 : 4-Methylenedioxy-β-benzaldoxime, when treated as above, gave after evaporation of the ether a viscous product which could not be crystallised. After hydrolysing with 2*N*-sodium hydroxide, saturating the solution with carbon dioxide, and extracting with ether, a small amount of 3 : 4-methylenedioxy-α-benzaldoxime was isolated, whilst on acidifying with hydrochloric acid and again extracting 3 : 4-methylenedioxybenzoic acid was obtained. From *m*-nitro-β-benzaldoxime, a crude product, m. p. 82—90°, was obtained; this was triturated with cold 2*N*-sodium hydroxide, and the residue identified as *m*-nitrobenzonitrile, formed from the β-acetyl derivative; the alkaline

solution, on treatment with carbon dioxide followed by ether extraction, gave *m*-nitro-α-benzaldoxime.

Action of Keten on Diphenylketoxime.—When diphenylketoxime was treated with keten, the ether solution on evaporation gave a mass of crystals, m. p. 72°, which after crystallisation from light petroleum gave pure acetyldiphenylketoxime, m. p. 74°. This was identified by comparison with a specimen obtained by the action of acetic anhydride on the ketoxime.

Acetyl Derivatives of β-Aldoximes.—Owing to the sensitivity of the acetyl-β-aldoximes, this work was carried out in a room free from acid fumes and illuminated by deep orange light only.

A solution of the β-aldoxime in a minimum of pure acetic anhydride was kept at room temperature for 5 minutes and then cooled to −20°; the solid was produced by scratching for some time. The suspension was poured on to a porous tile, and the solid crystallised by dissolving in dry benzene at room temperature and adding light petroleum slowly with constant scratching. The acetyl derivative thus produced was triturated with cold 2*N*-sodium hydroxide, kept for 5 minutes, and filtered. The solid residue was the nitrile; from the solution, yellow in the case of the nitro-compound, concentrated ammonium chloride precipitated the corresponding β-aldoxime. *o*-Nitro-β-benzaldoxime (m. p. 152°) gave *acetyl-o-nitro-β-benzaldoxime*, m. p. 73° (Found: N, 13·9. $C_9H_8O_4N_2$ requires N, 13·5%). The β-aldoxime recovered after trituration with sodium hydroxide had m. p. 146—149°. *m*-Nitro-β-benzaldoxime (m. p. 112°) gave a product, m. p. 96—98° (Hantzsch gives 75°) (Found: N, 14·2. Calc., N, 13·5%); the recovered β-aldoxime melted alone at 108—115°, and at 92° when mixed with the α-aldoxime. *p*-Nitro-β-benzaldoxime (m. p. 174°) gave a product, m. p. 96° (H. 75—76°) (Found: N, 14·4. Calc., N, 13·5%); the recovered β-aldoxime melted at 165—168°. 3 : 4-Methylenedioxy-β-benzaldoxime gave a product, m. p. 86° (H. 99°) (Found: N, 7·2. Calc., N, 6·7%); the recovered β-aldoxime melted at 135—138°.

No satisfactory results were given by the other methods described by Hantzsch (*Z. physikal. Chem.*, 1894, **13**, 509). The isolation of the β-aldoxime by treating with cold sodium hydroxide suggested that the supposed acetyl derivatives were contaminated with unchanged oxime. This was confirmed by the high percentage of nitrogen found. An alternative explanation is that the hydrolysis of the acetyl-β-oxime gave partly nitrile and partly β-oxime, the high analytical figures being due to contamination with nitrile. Judging from experience in the hydrolysis of other acyl-β-aldoximes, we think the second contingency the less likely.

Action of Ethyl Diazoacetate on Aldoximes.—Dry ethereal solutions

of *m*-nitro- and 3 : 4-methylenedioxy-α- and -β-benzaldoximes were treated with a slight excess of an ethereal solution of ethyl diazoacetate at room temperature for 48 hours. On removal of the solvent, the solutions of the α-aldoximes gave unchanged α-aldoxime, whilst those of the β-aldoximes gave a mixture of α- and β-aldoximes owing to isomeric change of the former into the latter.

Action of Phenylcarbimide on Aldoximes (compare Goldschmidt and others, *Ber.*, 1889, 22, 3112; 1890, **23**, 2136; 1891, **24**, 2546; 1893, **26**, 2087; Beckmann, *ibid.*, 1890, **23**, 3321; Brady and Dunn, J., 1916, **109**, 650; Brady and Thomas, J., 1922, **121**, 2100).—3 : 4-Methylenedioxy-α-benzaldoxime (7 g.) in a minimum of dry ether was treated with phenylcarbimide (5 g.), the precipitate that formed at once was separated, pressed on a porous tile, and washed with dry ether; it then melted at 78° (decomp.). A portion was treated with alcohol under reflux for an hour. On cooling, a small amount of diphenylcarbamide crystallised; the alcoholic filtrate from this was evaporated to dryness, and the residue crystallised from benzene and light petroleum, *carbanilino-3 : 4-methylenedioxy-α-benzaldoxime* being obtained as a white, micro-crystalline powder, m. p. 104° (decomp.) (Found: N, 9·7. $C_{15}H_{12}O_4N_2$ requires N, 9·8%).

From another portion, carbanilino-3 : 4-methylenedioxy-α-benzaldoxime was isolated by a method analogous to that used by Brady and Dunn for the *m*-nitro-derivative (J., 1916, **109**, 670; compare *idem*, J., 1914, **105**, 2877). The remainder of the crude product was hydrolysed with 2*N*-sodium hydroxide, when 3 : 4-methylenedioxybenzoic acid and 3 : 4-methylenedioxy-α-benzaldoxime were obtained, the former preponderating. There was, therefore, no doubt that the crude compound was a mixture of the two carbanilino-derivatives. When 3 : 4-methylenedioxy-β-benzaldoxime was similarly treated with phenylcarbimide, the precipitated *carbanilino-3 : 4-methylenedioxy-β-benzaldoxime* formed greenish-white plates, m. p. 84° (decomp.) (Found: N, 9·9. $C_{15}H_{12}O_4N_2$ requires N, 9·8%). Attempts to crystallise the compound from various solvents invariably led to isomeric change, the melting point falling. On treatment with warm 2*N*-sodium hydroxide it was rapidly decomposed; the insoluble residue consisted of 3 : 4-methylenedioxybenzonitrile and no α-oxime was detected; more prolonged hydrolysis gave the acid and ammonia. Similar results were obtained by the action of phenylcarbimide (6 g.) on *p*-nitro-α-benzaldoxime (4 g.), the mixture being kept for 5 minutes before the precipitate was separated. The crude product (m. p. 88°) on hydrolysis gave a mixture of acid and α-oxime, and on boiling with alcohol gave carbanilino-*p*-nitro-α-benzaldoxime,

m. p. 148—150°. With *p*-methoxy-α-benzaldoxime, the crude product (m. p. 74°) on hydrolysis gave acid and α-oxime, and on boiling with alcohol, the pure carbanilino-*p*-methoxy-α-benzaldoxime, m. p. 103°. In the case of *o*-nitro-α-benzaldoxime the addition of phenylcarbimide did not cause rapid precipitation of the carbanilino-derivative, so the solution was kept in the dark, out of contact with moisture, for 24 hours. The precipitate then melted at 105° and after one crystallisation from light petroleum gave pure carbanilino-*o*-nitro-α-benzaldoxime, m. p. 119°. The crude product on hydrolysis gave the α-oxime but no acid and seemed to contain no carbanilino-*o*-nitro-β-benzaldoxime, any which might have been formed originally having probably undergone isomeric change owing to the long period of keeping.

o-Methoxy-α-benzaldoxime, treated in an analogous manner to the above, behaved similarly. The crude product (m. p. 106°) on recrystallisation from benzene and light petroleum gave *carbanilino-o-methoxy-α-benzaldoxime*, white needles, m. p. 107° (decomp.) (Found: N, 10·5. $C_{15}H_{14}O_3N_2$ requires N, 10·4%). Hydrolysis of the crude product gave *o*-methoxy-α-benzaldoxime but no *o*-methoxybenzoic acid.

Action of Phenylcarbamyl Chloride on the Sodium Salts of α-Aldoximes.—The behaviour of two oximes, *viz.*, *m*-nitro- and *p*-methoxy-α-benzaldoxime, was investigated. The oxime was dissolved in dry ether, the calculated quantity of sodium dissolved in the minimum of alcohol added, the precipitated sodium salt washed with dry ether, and dried for a week in the dark over solid sodium hydroxide in a vacuum. The finely powdered salt was suspended in dry ether, in a well-stoppered vessel, and freshly prepared phenylcarbamyl chloride (1 mol.) added. The mixture was kept for 2 hours, with occasional shaking, filtered, and the solid extracted with cold chloroform. The residue, after being washed with water to remove sodium chloride, contained a very small quantity of diphenylcarbamide. In the case of *m*-nitro-α-benzaldoxime the chloroform solution was diluted with light petroleum; the precipitate formed consisted of slightly impure carbanilino-*m*-nitro-α-benzaldoxime. Alkaline hydrolysis gave only the α-oxime and no *m*-nitrobenzoic acid. In the case of *p*-methoxy-α-benzaldoxime, the chloroform was removed by a current of dry air; the crude product (m. p. 99°) was carbanilino-*p*-methoxy-α-benzaldoxime, alkaline hydrolysis giving the α-oxime and no acid.

Diphenylcarbamyl-o-methoxy-β-benzaldoxime.—A solution of sodium (0·76 g.) in the minimum of absolute alcohol was added to a solution of *o*-methoxybenzaldoxime (5 g.) in dry ether, followed by a large excess of ether. The precipitated sodium salt was washed

with ether and dried in a vacuum over solid sodium hydroxide, suspended in dry chloroform with diphenylcarbamyl chloride (7·7 g.), and heated under reflux for 4 hours. The sodium chloride formed was separated, and the filtrate evaporated at room temperature. The oil was treated with 10 c.c. of 2*N*-sodium hydroxide and 10 c.c. of ether, the whole being well stirred together. The colourless crystals separating were collected, washed with a little ether, then with water, and dried in a vacuum. On crystallising from light petroleum to which about 10% of benzene had been added to increase the solvent action, *diphenylcarbamyl-o-methoxy-β-benzaldoxime* was obtained in small, colourless needles, m. p. 124° (decomp.) (Found: N, 8·2. $C_{12}H_{18}O_3N_2$ requires N, 8·1%). On hydrolysis with sodium hydroxide under reflux, ammonia was evolved, and diphenylamine and *o*-methoxybenzoic acid were isolated from the solution.

Action of Ethyl Chloroformate on α- and β-Cinnamaldoximes (compare Brady and McHugh, J., 1923, **123**, 1190).—α-Cinnamaldoxime (1 g.) was dissolved in 2*N*-sodium hydroxide (20 c.c.), and ethyl chloroformate (0·8 g.) added with cooling and shaking. The precipitate was washed with water, pressed on a tile, washed with a very little ether, and crystallised from benzene and light petroleum, when *carbethoxy-α-cinnamaldoxime* was obtained in pale yellow crystals, m. p. 64° (Found: N, 6·6. $C_{12}H_{13}O_3N$ requires N, 6·4%). On hydrolysis by heating on the water-bath for an hour with 2*N*-sodium hydroxide and saturating with carbon dioxide, the α-oxime was recovered. When β-cinnamaldoxime was treated under the same conditions with ethyl chloroformate, an uncrystallisable oil was obtained, which was identified as cinnamonitrile by its boiling point and by hydrolysis to ammonia and cinnamic acid.

Action of α-Naphthylcarbimide on α- and β-Cinnamaldoximes (compare Brady and Ridge, J., 1923, **123**, 2163).—α-Cinnamaldoxime in dry ether was mixed with an equal weight of α-naphthylcarbimide in a stoppered vessel; after 1 hour, glistening, pale yellow plates of *α-naphthylcarbamyl-α-cinnamaldoxime* separated, m. p. 152° (decomp.). Crystallisation from acetone and water did not alter the melting point (Found: N, 9·0. $C_{20}H_{16}O_2N_2$ requires N, 8·9%). Hydrolysis with hot 2*N*-sodium hydroxide for an hour gave α-naphthylamine, *s*-di-α-naphthylcarbamide, and α-cinnamaldoxime (see Brady and Ridge, *loc. cit.*, for a general method of separation).

To a solution of β-cinnamaldoxime in dry ether was added an equal weight of α-naphthylcarbimide. After keeping for 30 minutes, glistening, deep yellow plates were deposited which, after being washed with dry ether, consisted of *yellow α-naphthylcarbamyl-β-*

cinnamaldoxime, m. p. 125° (decomp.) (Found : N, 9·0. $C_{20}H_{16}O_2N_2$ requires N, 8·9%). This compound could not be crystallised. When it was dissolved in cold acetone, and water added cautiously, rectangular plates of *colourless α-naphthylcarbamyl-β-cinnamaldoxime* separated, m. p. 125° (decomp.) (Found : N, 8·9%) (compare Brady and Thomas, J., 1922, **121**, 2105, for similar behaviour with phenylcarbimide). A mixture of the yellow and white modifications still melted and decomposed at 125°, and both forms on hydrolysis with 2*N*-sodium hydroxide for an hour gave α-naphthylamine, *s*-di-α-naphthylcarbamide, ammonia, and cinnamic acid.

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CCCXXIX.—*The Isomerism of the Oximes. Part XXIV. 4-Methoxy-3-methyl-, 3-Nitro-4-methyl-, and Some ortho-Substituted Benzaldoximes.*

By OSCAR L. BRADY, ANTOINETTE N. COSSON, and ARTHUR J. ROPER.

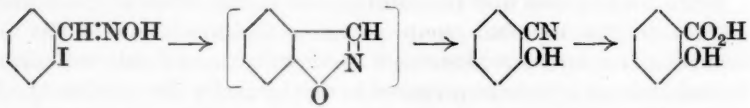
THIS communication is a continuation of those dealing with the influence of one or more substituents in the benzene nucleus on the formation of the unstable β-oxime (see this vol., p. 2415, for footnote explaining the nomenclature adopted) (Brady and Dunn, J., 1914, **105**, 821, 2409, 2872; 1915, **107**, 1858; 1916, **109**, 667; Wentworth and Brady, J., 1920, **117**, 1040; Brady and Truszkowski, J., 1923, **123**, 2434; Brady and Manjunath, J., 1924, **125**, 1060).

Some doubt exists how far substitution in the ortho-position with respect to the oximino-group prevents the formation of the β-isomeride; *o*-nitrobenzaldoxime, 2 : 4-dimethyl- and 2-chloro-3-nitrobenzaldoximes have been prepared in two forms by the usual method, and *o*-chloro-β-benzaldoxime was obtained by Behrend and Nissen (*Annalen*, 1892, **269**, 390) by the action of alkalis on bisnitrosyl-*o*-chlorobenzyl and by McHugh and one of us (J., 1924, **125**, 547) by the action of ultra-violet light on the α-isomeride, but attempts to obtain it through the hydrochloride were unsuccessful (Dollfus, *Ber.*, 1892, **25**, 1923). Similarly, although 2 : 5-dimethyl-β-benzaldoxime was obtained by Scholl and Kačer (*Ber.*, 1903, **36**, 322) by the action of mercuric fulminate on *p*-xylene in presence of aluminium chloride, it could not be prepared from the α-oxime through the hydrochloride (Francesconi and Mundici, *Gazzetta*, 1902, **32**, ii, 467). Dollfus (*loc. cit.*) failed to convert *o*-methylbenzaldoxime into the β-form and many attempts to prepare the β-isomeride of *o*-methoxybenzald-

oxime under widely varying conditions have been made, but without success, by one of us and others; failure in the latter case is the more surprising since *p*-methoxy-β-benzaldoxime is exceptionally stable.

The behaviour of *o*-halogeno- and *o*-ethoxy-benzaldoximes has now been studied. *o*-Chloro- and *o*-bromo-α-benzaldoximes were converted into their β-isomerides through the hydrochloride under suitable experimental conditions, but no β-compound could be obtained from *o*-iodo- and *o*-ethoxy-α-benzaldoximes. It is notable that the β-isomerides of ortho-substituted compounds can in some cases be prepared only under special experimental conditions but that when obtained they do not appear to be unusually unstable. There seems, therefore, to be no justification for assuming that failure to obtain β-isomerides from certain aldoximes is due to excessive instability of that form, and we are of opinion that the explanation must be sought either in the constitution of the hydrochloride or in some influence hindering the rearrangement of the hydrochloride; this view is supported by the formation of β-derivatives from oximes known only in the α-form, *e.g.*, carbanilinodimethylamino-β-benzaldoxime (Brady and Dunn, J., 1914, **105**, 2877). In general, it may be said that ortho-substitution does not necessarily inhibit the formation of the β-isomeride, but produces a distinct hindering effect.

The action of alkalis on *o*-halogenobenzaldoximes has been investigated (compare Brady and Bishop, this vol., p. 1357). The results are given in the experimental section; the formation of salicylic acid from *o*-iodo-α-benzaldoxime probably takes place through the benz*iso*oxazole:



It is unfortunate that *o*-iodo-β-benzaldoxime could not be obtained, because we were unable to test further the results of Bishop and one of us on the relative ease of formation of the *iso*-oxazole ring from the two isomerides.

EXPERIMENTAL.

o-*Chloro*-α- and -β-*benzaldoximes*.—Solutions of hydroxylamine hydrochloride (12 g. in 200 c.c. of water) and sodium hydroxide (18 g. in 200 c.c. of water) were mixed with cooling, and *o*-chlorobenzaldehyde (20 g.) was added. After 10 minutes, the mixture was shaken with ether to extract impurities such as *o*-chlorobenzyl

chloride (which are frequently present in the aldehyde). The α-oxime was precipitated from the alkaline solution with carbon dioxide, crystallised from benzene, dissolved in concentrated hydrochloric acid, and the solution saturated with hydrogen chloride and poured slowly into a large excess of 2*N*-sodium carbonate with very vigorous stirring. The oxime thus precipitated was washed, rapidly dried (m. p. 62—96°) on a porous tile, dissolved in benzene, and light petroleum added; the β-oxime then crystallised, m. p. 101—103° (Behrend and Nissen, *loc. cit.*, give m. p. 98—102°, and Brady and McHugh, *loc. cit.*, 110°).

When a solution of the α-oxime in dry ether was saturated with hydrogen chloride, no precipitate appeared, but on scratching for a few minutes a *hydrochloride* separated as a white, crystalline powder, m. p. 108° (decomp.) (Found: Ionisable Cl, 17·9. $C_7H_7ONCl_2$ requires ionisable Cl, 18·5%). On decomposition with 2*N*-sodium carbonate this regenerated the α-oxime, and a similar result was obtained when boiling benzene was employed as solvent (compare Brady and Dunn, J., 1923, **123**, 1783).

o-*Bromo*-α-*benzaldoxime*.—The preparation of *o*-bromobenzaldehyde from *o*-bromotoluene by Etard's reaction having given very poor yields, the following, more satisfactory, method was used. Acetic anhydride (40 g.), glacial acetic acid (30 g.), concentrated sulphuric acid (15 g.), and *o*-bromotoluene (5 g.) were mixed cautiously in the order named, cooled to 0°, chromium trioxide (10 g.) in glacial acetic acid (30 g.) was slowly added, the temperature being kept below 10°, and the mixture was poured on to crushed ice. The solid produced, on crystallising from alcohol, gave o-*bromobenzylidene diacetate* in colourless crystals, m. p. 84—86° (Found: Br, 27·8. $C_{11}H_{11}O_4Br$ requires Br, 27·9%). The diacetate was boiled under reflux for 2 hours with concentrated hydrochloric acid, and the solution diluted and shaken with ether. The crude aldehyde isolated from the extract was oximated by the method described above for the *o*-chloro-compound; by crystallising the product from benzene, pure *o*-bromo-α-benzaldoxime was obtained, m. p. 102° (compare V. Meyer, *Ber.*, 1892, **25**, 2188). This was oriented in the usual way by means of acetic anhydride. *Acetyl*-o-*bromo*-α-*benzaldoxime* crystallises from light petroleum or from acetone and water in colourless plates, m. p. 66° (Found: N, 5·8. $C_9H_8O_2NBr$ requires N, 5·8 %).

o-*Bromo*-β-*benzaldoxime*.—A solution of *o*-bromo-α-benzaldoxime in chloroform was saturated with hydrogen chloride. No hydrochloride was precipitated, so the solution was added to excess of vigorously stirred 2*N*-sodium hydroxide, the alkaline layer separated and rapidly saturated with carbon dioxide. The precipitated oxime

was rapidly dried on a porous tile and crystallised from benzene, o-*bromo*-β-*benzaldoxime* being obtained in colourless needles, m. p. 126° (Found: N, 7·2. C_7H_6ONBr requires N, 7·0%). On treatment with acetic anhydride and sodium carbonate, this gave *o*-bromobenzonitrile, m. p. 51°. No conversion of the α- into the β-oxime was effected by dissolution in concentrated hydrochloric acid, etc. A solution of the α-oxime in ether saturated with hydrogen chloride gave, on scratching, a ***hydrochloride*** as a white, crystalline powder, m. p. 115° (decomp.) (Found: Cl, 15·3. $C_7H_7ONClBr$ requires Cl, 15·0%); this on decomposition with sodium carbonate regenerated the α-oxime.

o-*Iodo*-α-*benzaldoxime*.—Oxidation of *o*-iodotoluene by the method described above in the case of *o*-bromotoluene gave no *o*-iodobenzylidene diacetate. The aldehyde was therefore prepared by Friedländer's method (*Ber.*, 1884, **17**, 456) and the oxime by Patterson's (J., 1896, **69**, 1002). The latter, on treatment with ethereal hydrogen chloride, gave the hydrochloride as a yellow, crystalline powder, m. p. 100—102° (decomp.), but this on decomposition regenerated the original α-oxime. The other methods, described above, also failed to bring about conversion.

Action of Alkalis on o-*Halogenobenzaldoximes*.—*o*-Iodo-α-benzaldoxime was boiled for 2 hours under reflux with 20 times its weight of 30% sodium hydroxide. From a portion of the solution, acidified with dilute nitric acid, silver nitrate produced a copious precipitate of silver iodide. The remaining portion was acidified with dilute sulphuric acid and extracted with chloroform, the extract was washed with very dilute sulphurous acid to remove iodine and then evaporated. The solid residue on crystallisation from water gave salicylic acid, which was identified by direct comparison, by its reaction with ferric chloride, and by the formation of methyl salicylate. *o*-Chloro-α- and β-benzaldoximes and *o*-bromo-α-benzaldoxime gave no ionised halogen under the above conditions; *o*-bromo-β-benzaldoxime lost some halogen, the solution acidified with dilute nitric acid giving a very pronounced opalescence with silver nitrate, but the amount of decomposition was insufficient for salicylic acid to be isolated.

o-*Ethoxy*-α-*benzaldoxime*.—The oxime was prepared in the same way as [*o*-chloro-α-benzaldoxime and crystallised from light petroleum; m. p. 58° (Löw, *Monatsh.*, 1891, **12**, 395). Attempts to obtain the β-isomeride by the methods here described were uniformly unsuccessful, the pure α-oxime being invariably recovered.

4-*Methoxy*-3-*methyl*-α-*benzaldoxime*.—Solutions of hydroxylamine hydrochloride (15 g. in 50 c.c. of water) and sodium hydroxide (20 g. in 150 c.c. of water) were mixed with cooling, and 4-methoxy-

3-methylbenzaldehyde (30 g.) was added. The aldehyde dissolved after 15 minutes' shaking, and after a further 30 minutes the solution was saturated with carbon dioxide; the oil thus precipitated slowly solidified. After being dried, it was crystallised by dissolving in light petroleum at 60° and cooling rapidly, when the oxime was obtained, m. p. 71° (Gattermann, *Annalen*, 1907, **357**, 355, gives m. p. 68—70°, but confesses to considerable difficulty in purifying his product). During the orientation of the compound in the usual way, *acetyl-4-methoxy-3-methyl-α-benzaldoxime* was obtained; it crystallised from light petroleum in white plates, m. p. 70° (Found: N, 7·0. $C_{11}H_{13}O_3N$ requires N, 6·8%).

4-Methoxy-3-methylbenzonitrile.—The α-oxime was boiled for 90 minutes under reflux with excess of acetic anhydride, and the solution thus obtained was cooled and poured into 2*N*-sodium carbonate. When the excess of anhydride had been decomposed, the mixture was placed on ice and left over-night; the oil had then solidified. A solution of the solid in absolute alcohol, on evaporating slowly, deposited *4-methoxy-3-methylbenzonitrile* in colourless needles, m. p. 51—52° (Found: N, 9·7. C_9H_9ON requires N, 9·5%). This was hydrolysed by boiling for 2 hours with 2*N*-sodium hydroxide, the solution cooled, acidified with hydrochloric acid, and the precipitate crystallised from alcohol, *4-methoxy-3-methylbenzoic acid* being thus obtained in small, colourless needles, m. p. 192° (Found: C, 64·9; H, 6·2. $C_9H_{10}O_3$ requires C, 65·1; H, 6·0%). This acid was also obtained, but in poor yield, by heating the aldehyde for an hour with ammoniacal silver nitrate, filtering the hot solution, and acidifying the filtrate with nitric acid.

4-Methoxy-3-methyl-β-benzaldoxime.—A solution of the α-oxime in warm chloroform was saturated during 15 minutes with hydrogen chloride. The precipitated hydrochloride, a white, crystalline powder, m. p. 171° (decomp.) (Found: Cl, 17·4. $C_9H_{12}O_2NCl$ requires Cl, 17·6%), was dissolved in excess of cold 2*N*-sodium hydroxide and a saturated solution of ammonium chloride added, when *4-methoxy-3-methyl-β-benzaldoxime* was precipitated; it crystallised from acetone and water in microscopic, colourless needles, m. p. 121° (Found: N, 8·3. $C_9H_{11}O_2N$ requires N, 8·5%). When its configuration was determined with acetic anhydride, this oxime gave 4-methoxy-3-methylbenzonitrile.

3-Nitro-4-methyl-α-benzaldoxime.—Hydroxylamine hydrochloride (8 g. in 25 c.c. of water) was mixed with sodium hydroxide (10 g. in 75 c.c. of water), and 3-nitro-4-methylbenzaldehyde (16 g.) in a minimum of warm alcohol added. After 2 hours, the solution was saturated with carbon dioxide, and the precipitate, after washing, crystallised from alcohol; *3-nitro-4-methyl-α-benzaldoxime* was then

obtained in pale yellow needles, m. p. 118—120° (Found : N, 15·6. $C_8H_8O_3N_2$ requires N, 15·6 %). Cold acetic anhydride and sodium carbonate solution gave *acetyl-3-nitro-4-methyl-α-benzaldoxime*, which separated from acetone and water in colourless crystals, m. p. 104° (Found : N, 12·5. $C_{10}H_{10}O_4N_2$ requires N, 12·2%). On hydrolysis, it regenerated the original oxime.

3-Nitro-4-methyl-β-benzaldoxime.—A solution of the α-oxime in warm dry chloroform, on saturation with hydrogen chloride, gave a white, crystalline precipitate of the *hydrochloride*, m. p. 140° (decomp.) (Found : Cl, 16·4. $C_8H_9O_3N_2Cl$ requires Cl, 16·6%). This was rapidly dissolved in 2*N*-sodium hydroxide (3 equivs.), and a saturated solution of ammonium chloride added ; the precipitate of *3-nitro-4-methyl-β-benzaldoxime* separated from acetone and water in colourless crystals, m. p. 135° (Found : N, 15·5. $C_8H_8O_3N_2$ requires N, 15·6%). With acetic anhydride and sodium carbonate solution, this oxime gave 3-nitro-4-methylbenzonitrile.

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CCCXXX.—*The Periodic Crystallisation of Pure Substances.*

By ERNEST SYDNEY HEDGES and JAMES ECKERSLEY MYERS.

SEVERAL investigators have observed the production of periodic structures resembling the Liesegang phenomenon in the crystallisation of thin films of pure substances from a melt or from solution. Thus, Alexéev (*J. Russ. Phys. Chem Soc.*, 1906, **38**, 1120) reports that ethyl ethanetetracarboxylate, benzophenone, and coumarin crystallise in concentric zones when a thin layer of the molten substance is allowed to cool. Rhythmic crystallisation of sulphanilic acid–sulphuric acid mixtures, *p*-toluonitrile, salol, and methylsalicylic acid has formed the subject of an investigation by Schubert (*Kolloid-Z.*, 1924, **35**, 219), whilst Garner and Randall (J., 1924, **125**, 369) have shown that thin films of certain higher fatty acids crystallise in the form of waves. Vorländer and Ernst (*Z. physikal. Chem.*, 1919, **93**, 521) and Kägi (*Helv. Chim. Acta*, 1923, **6**, 264) observed crystallisation in concentric rings of other organic substances from a state of solution. The rhythmic crystallisation of thin films of molten sulphur has been investigated by Fischer-Treuenfeld (*Kolloid-Z.*, 1915, **16**, 109) and by Köhler (*ibid.*, 1915, **17**, 10). The cause of the phenomenon has been attributed by Alexéev (*loc. cit.*) to local alterations in surface tension due to the

FIG. 1.

The periodic crystallisation of benzoic acid from sulphuric acid–ethyl alcohol solution.

FIG. 2.

The effect is not confined to a surface film, but extends throughout the whole mass.

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liberation of heat of crystallisation, and this view has also been urged by some more recent investigators.

Some cases are on record of the periodic crystallisation of inorganic salts from aqueous solution, the best-known instance being potassium dichromate (Miers, *Min. Mag.*, 1908, **15**, 39). Similar effects have been observed with sodium carbonate by Hofsäss (*Z. physikal. Chem.*, 1919, **93**, 754).

Experimental.

The present authors have carried out some experiments with thin films of solutions of chrome alum and of barium nitrate. In these cases, the best method of procedure is as follows: a drop of an aqueous solution of the substance saturated at room temperature is spread on a microscope slide, which is then warmed gently over a Bunsen flame and quickly transferred to the microscope. It is essential that the slide be carefully cleaned to facilitate spreading of the drop. The alternate periods of rapid and slow growth starting from the edge of the drop and producing corresponding rings of branched growths and geometrical crystals of potassium dichromate have been described by Miers (*loc. cit.*). With chrome alum, crystallisation proceeds much more slowly with the formation of a metastable, optically active, spherulitic form (compare Miers, *Min. Mag.*, 1906, **14**, 134). The bands consist of alternate zones of small and large spherulites. Crystallisation proceeds initially at a fairly rapid rate with the formation of a large number of small particles, and then at a slower rate with formation of a smaller number of large particles, the two speeds thereafter alternating. Similar observations were made with barium nitrate.

These observations are analogous to those of Hatschek (2nd Brit. Assoc. Colloid Report, 1918) on the distribution of particles with respect to size in rhythmic precipitation structures. In general, the periodic structure only appears in these cases when the film of liquid is very thin and the rate of crystallisation fairly rapid; the distance between the rings decreases for thinner films and with increasing rate of crystallisation. The view put forward by Miers is that crystallisation of the first ring takes place by inoculation when part of the solution reaches the labile state by cooling: as soon as this rapid growth has reduced the concentration of the solution in the immediate vicinity to the metastable condition, the crystals continue to grow slowly; in the meantime, the next ring of solution is becoming labile by evaporation and cooling and the rapid crystallisation recommences at some point. Such an explanation seems to meet the case of potassium dichromate, but it

is doubtful whether its applicability is universal. The authors would point out that at least in the case of chrome alum the periodicity is only observed when the metastable, spherulitic form appears, and this suggests a link with other types of physicochemical periodicity (Hedges and Myers, J., 1924, **125**, 604, 1282; this vol., pp. 445, 1013), which are associated with surfaces which are believed to be in a metastable state. It seems probable that periodic phenomena are a general characteristic of such metastable systems.

The foregoing instances are characterised by conditions where a small quantity of substance exhibits a large surface, but this does not appear to be essential for rhythmic crystallisation. The present authors have observed that benzoic acid crystallises in a very beautiful wave-form from mixtures of sulphuric acid and ethyl alcohol. This effect is well portrayed in Fig. 1. It is not a surface formation, but affects the whole mass of substance, the layers being arranged round the crystallisation nuclei like the coats of an onion. Fig. 2, which is another photograph of the same specimen taken from a different aspect, illustrates the solidity of the effect.

This phenomenon can be reproduced by warming 5 g. of benzoic acid with 12—20 c.c. of an equal-volume mixture of sulphuric acid and ethyl alcohol and setting aside to cool. The crystallisation starts from nuclei and spreads radially with constant decrease in the distance between successive rings. Although in almost all cases of rhythmic crystallisation the distance between successive rings is considerably less than a millimetre, in fact being often observable only by means of a lens, in the present case the effect is on a comparatively enormous scale and the rings in the specimen photographed were about a centimetre apart. Examination shows the layers to consist of closely packed crystals of benzoic acid separated by spaces containing mostly solution with some benzoic acid crystals sufficient to give rigidity to the whole. Crystallisation of benzoic acid from sulphuric acid or ethyl alcohol alone does not give rise to such periodic formations.

The authors wish to express their best thanks to Sir Henry A. Miers, F.R.S., in whose laboratory some of the experiments were carried out.

THE UNIVERSITY, MANCHESTER. [*Received, July* 31*st*, 1925.]

CCCXXXI.—*The Rotation-Dispersion of Optically Active Compounds. Dimethoxysuccinates and Pyridine.*

By Thomas Stewart Patterson and James Davidson Fulton.

Modern work on optical activity has disclosed, in general, the very important fact that if, under two entirely different sets of circumstances (temperature, concentration, solvent), the rotations for some particular colour, say sodium yellow, are the same, then the rotations for all the other colours also will be the same or very nearly the same, each to each. This is the lesson of the characteristic diagram, and it holds not merely for one and the same substance in different sets of circumstances, but also for derivatives of that active substance.

From the characteristic diagram we are thus able to foretell for a group of related compounds that if by varying the external conditions we can produce a certain rotation for one colour of light, the rotations for other colours will have certain definite values. But the characteristic diagram, unfortunately, does not indicate the physical conditions necessary to bring about a certain effect, or how they may be produced. Further, the characteristic diagram, although of a remarkably general character, is only an approximation, and, as far as can be judged at present, there are, probably, definite limits to its application. Thus for many substances, the rotation passes through a maximum or minimum value with change of temperature, and the data at present available are insufficient to show whether the rotation values on both sides of such a maximum fall upon a single characteristic diagram or not. It is clear that the difference between the rotation values for two colours of light—what may be called the dispersion—is directly proportional to either value, if calculated from the point of intersection for these two colours—the rational zero. Using the rational zero, a dispersion coefficient may be arrived at which shows very fair constancy under widely differing circumstances and may in future prove to be definitely characteristic of a particular substance or group of substances.

The experimental difficulties encountered in examining the rotation of an active substance over a wide range of temperature are considerable, and therefore only a comparatively short part of the T–R curves for most active compounds has been ascertained. It has been suggested, however, by one of us, that this difficulty can be at least partly overcome by piecing together T–R curves for solutions of the active compound in question, or derivatives of

it, just as a characteristic diagram is constructed by piecing together data of different kinds—the evidence being indeed just the same in both cases. The question, similar to that already referred to, then arises, as to whether the dispersion-coefficient derived from such T–R curves would have the same value as for the mother-substance, when calculated from the rational zero. It was with a view to collect further evidence of this kind that the work described below was undertaken.

For our purpose it is desirable to study substances the rotations of which vary as much as possible with change of external conditions. Some previous work had shown that benzyl tartrate has a fairly high rotation, and, moreover, that the maximum in the T–R curve lies at a moderate and easily ascertainable temperature (J., 1913, **103**, 148). We therefore thought it worth while to examine in the first place dibenzyl dimethoxysuccinate, hoping that its rotation would be both high and easily variable.

Dibenzyl dimethoxysuccinate was prepared from *d*-dimethoxysuccinic acid (J., 1901, **79**, 959) (1 mol.) by heating with pure benzyl alcohol (4 mols.) at 120° for about 16 hours and allowing the water formed to distil off. The excess of alcohol was removed under diminished pressure; the crude ester was washed with dilute sodium carbonate solution, taken up in chloroform, dried over calcium chloride, and distilled (yield 70%). It was slightly coloured and fairly mobile. Purified by careful distillation, it boiled at 180—190°/3 mm.; $n_D^{19^\circ} = 1{\cdot}5321$ (Found: C, 66·8; H, 6·1. $C_{20}H_{22}O_6$ requires C, 67·0; H, 6·1%).

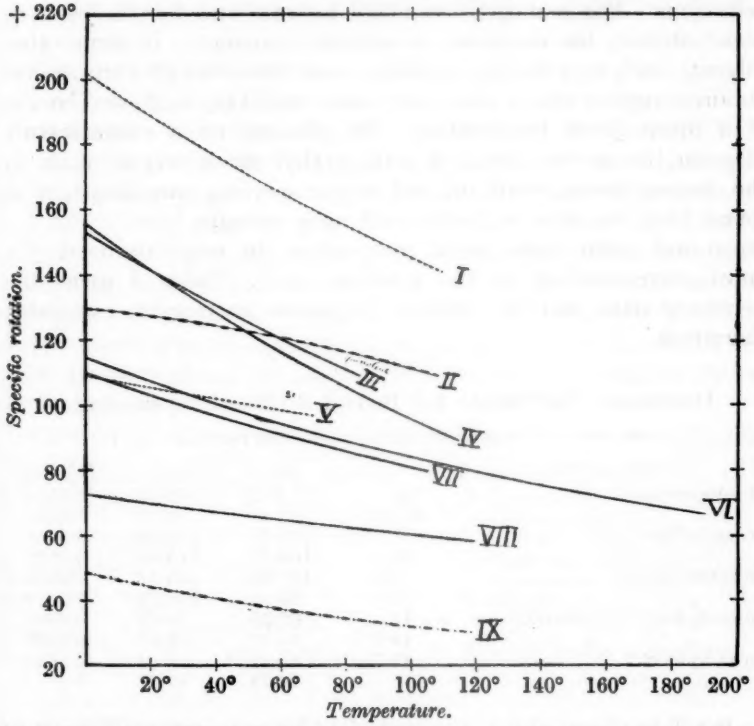
The rotation of this ester was examined for six different wavelengths of light at temperatures ranging from 0—100°. In the case of the homogeneous substance, the examination was continued up to 174°. The results are shown in Fig. 1, which gives the curves obtained for mercury green light alone. It will be seen that the specific rotation of the homogeneous benzyl dimethoxysuccinate, which has a high value of about 115° at zero, gradually falls to reach a value of 68° at a temperature of 180°, the appearance of the curve suggesting a maximum value at some temperature considerably below zero and a minimum value at a temperature possibly in the neighbourhood of 250°.

The influence of solvents upon this ester is also apparent from the diagram. Acetylene tetrabromide lowers the rotation of the ester considerably. *m*-Xylene lowers it only slightly. Nitrotoluene and quinoline both raise the rotation markedly. The general appearance of the curves is very similar to what has been observed already for the rotation of ethyl tartrate, but the displacement of a maximum or minimum value is not so obvious.

For purposes of comparison, the temperature–rotation curves of some other related compounds were examined. Benzyl tartrate (J., 1913, **103**, 176) in quinoline has a much lower rotation than benzyl dimethoxysuccinate, but the general appearance of the curve is similar. The rotation of methyl dimethoxysuccinic acid

FIG. 1.

Influence of solvents on the rotations of various related compounds.



I. d-*Dimethoxysuccinic acid in pyridine*, p = 7·8435. II. *Methyl* d-*dimethoxysuccinate in quinoline*, p = 5·5020. III. *Benzyl* d-*dimethoxysuccinate in quinoline*, p = 5·1758. IV. *Benzyl* d-*dimethoxysuccinate in* o-*nitrotoluene*, p = 4·860. V. d-*Dimethoxysuccinic acid in acetone*, p = 15·982. VI. *Benzyl* d-*dimethoxysuccinate* (*homogeneous*). VII. *Benzyl* d-*dimethoxysuccinate in* m-*xylene*, p = 6·6875. VIII. *Benzyl* d-*dimethoxysuccinate in acetylene tetrabromide*, p = 3·0660. IX. *Benzyl tartrate in quinoline*, p = 9·4489.

in acetone is considerably higher, but the curve is again of a similar form, the rotation gradually diminishing as the temperature rises. Dimethoxysuccinic acid dissolved in pyridine gives again a *T–R* curve of a similar form, the rotation, however, being much higher. Methyl dimethoxysuccinate dissolved in quinoline, shows, for all the colours of light examined, a behaviour suggesting a maximum

at a temperature in the neighbourhood of zero. It is clear, however, that any fundamental type of curve for these different compounds is not displaced to nearly so great an extent as is the curve for ethyl tartrate. All these curves, with the possible exception of that for methyl dimethoxysuccinate in quinoline, suggest that the T–R curve would rise to a maximum at lower temperatures than those examined. Homogeneous ethyl tartrate and the same ester dissolved in a number of solvents exhibited just the opposite behaviour. For homogeneous ethyl tartrate and for the ester in some solvents, the maximum is actually apparent. In some other solvents such as quinoline, pyridine, and benzaldehyde, the curves obtained suggest that a maximum value would lie, in these solvents, at a much lower temperature. On plotting on a characteristic diagram the results obtained with methyl dimethoxysuccinate in the homogeneous condition and in the solvents mentioned, it is found that the data lie fairly well upon straight lines, which for green and yellow light would intersect in the neighbourhood of a point corresponding to the rotation + 9°. Table I gives the necessary data and the rational dispersion coefficients calculated therefrom.

TABLE I.

Dispersion Coefficients for Benzyl *d*-Dimethoxysuccinate.

$[\alpha]_y/[\alpha]_g$ is the rational dispersion coefficient for the rational zero $[\alpha] = +9°$.

Physical state.	$t°$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_y/[\alpha]_g$.
Homogeneous	100°	72·72°	82·84°	0·8630
,, ...	139·5	65·98	74·82	0·8659
In quinoline	0	134·9	154·59	0·8648
,, ...	69·2	100·4	115·02	0·8621
In nitrotoluene	13·6	127·06	145·51	0·8648
,, ...	72	95·13	108·25	0·8678
In acetylene tetrabromide ...	14	62·25	70·62	0·8642
,, ,, ...	44·2	58·77	66·63	0·8636
In *m*-xylene	43·7	83·11	95·04	0·8614
,, ...	69	76·73	87·31	0·8649

It will be observed that the coefficient is very constant, differences only occurring in the third decimal place. Its mean value is 0·8642.

In Table II are shown similar dispersion coefficients for the other substances which have been examined and it will be seen that the dispersion coefficient is slightly higher than before, having a mean value of about 0·876 when the values are calculated from a rational zero of + 9°.

The data of Tables I and II have reference, as will be apparent from Fig. 1, to a region of the T–R curves to the right of the maximum. It is of interest now to compare them with similar data for ethyl tartrate applying to T–R curves on the other side of

TABLE II.

Dispersion Coefficients for *d*-Dimethoxysuccinic Acid and for Methyl *d*-Dimethoxysuccinate.

$[\alpha]_\gamma/[\alpha]_\beta$ is the rational dispersion coefficient for the rational zero $[\alpha] = +9°$.

Physical state.	$t°$.	$[\alpha]_\gamma$.	$[\alpha]_\beta$.	$[\alpha]_\gamma/[\alpha]_\beta$.
d-Dimethoxysuccinic acid in pyridine	0°	180·96°	204·38°	0·8801
d-Dimethoxysuccinic acid in pyridine	69	142·37	161·24	0·8761
In acetone	12	94·00	106·29	0·8737
,,	30·5	91·96	103·75	0·8756
Methyl *d*-dimethoxysuccinate in quinoline	0	114·55	129·40	0·8766
Methyl *d*-dimethoxysuccinate in quinoline	67	105·67	119·39	0·8757

the maximum, namely, between temperatures of 40° and 140° (J., 1916, **109**, 119). The rational zero then found was + 7·92°, very close, therefore, to that (+ 9°) obtained from our present experiments. The mean value of the rational dispersion coefficient was 0·8660, again close to the values found above. Our results lend support, therefore, to the idea that even when the data are taken from *T*–*R* curves apparently on different sides of the maximum rotation, the rational dispersion-coefficient shows something like a real constancy.

Rotation of Nicotine.

Since it was not found possible to vary the rotation of the dimethoxysuccinates as much as we had hoped, we next undertook an examination of nicotine, the rotation of which is known to vary to some considerable extent, but has not hitherto been examined very completely in regard to change of colour, temperature, and concentration. Previous workers have given the following values for the constants of the homogeneous substance :

	$[\alpha]_D^{20°}$.	$d_4^{20°}$.
Landolt (" Das Optische Drehungsvermögen," 2nd ed., 1898, p. 159)	161·55°	1·01101
Gennari (*Z. physikal. Chem.*; 1896, **19**, 130)	162·84	1·01071
Winther (*ibid.*, 1907, **60**, 563)	163·85	—
Jephcott (J., 1919, **105**, 105)	168·61	1·00925

The first three purified their nicotine by vacuum distillation only. In the last case the nicotine was purified by means of the zinc chloride double salt (Vohl, *J. pr. Chem.*, 1870, **2**, 331). We used 95% nicotine, purified it by preparation of the double salt with zinc chloride, decomposed this in sodium hydroxide, dried the nicotine over solid sodium hydroxide, and then distilled it under reduced pressure, using a Claisen flask with a long side arm, and a receiver of the type described in *J. Soc. Chem. Ind.*, 1924,

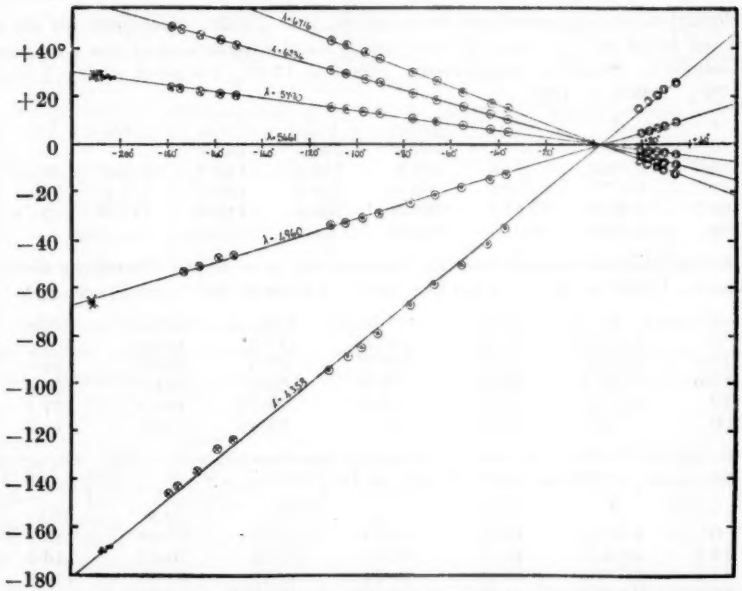
43, 283, thus avoiding completely any contact of the hot vapour or liquid with cork or rubber. A colourless, odourless liquid was obtained. Two separate preparations gave: (1) $[\alpha]_D^{20^\circ}$ 168·02°, $d_4^{20^\circ}$ 1·0095; (2) $[\alpha]_D^{20^\circ}$ 167·78°, $d_4^{20^\circ}$ 1·0100. The homogeneous substance was then examined for six colours of light over a range of temperature from 0—100°, in polarimeter tubes having a side arm to allow of expansion of the liquid. In order to prevent oxidation of the nicotine by air, a slow current of hydrogen was passed into the side arm. This proved entirely satisfactory; no coloration of the solution due to oxidation of the nicotine took place even at 100°, at which temperature oxidation in presence of air is extremely rapid. The data obtained, when plotted on a diagram, indicate that the change of rotation of nicotine with temperature is only slight, but the shape of the curves suggests the occurrence of a minimum at a temperature probably in the neighbourhood of 170° or thereabouts.

Nicotine was then examined in a number of solvents. *o*-Nitrotoluene as a solvent diminishes to some slight extent the rotation of nicotine, which is then almost unaffected by temperature change. In ethyl acetate, the rotation is depressed almost to the same extent, but not quite so much as in *o*-nitrotoluene, the temperature coefficient being again very small. α-Bromonaphthalene raises the rotation of nicotine, the temperature coefficient becoming somewhat greater at the same time—the rotation becomes more negative as the temperature rises. In quinoline, nicotine has a rotation at zero of — 152°. It falls steadily until at 100° the value is — 179°. This temperature–rotation curve is therefore quite in agreement with the others. Water raises the rotation of nicotine considerably, the value at zero being — 90°. Heating lowers the value much as in quinoline. Formamide also was used as a solvent, and in this case the rotation fell from — 35·6° at zero to — 77·5°. The formamide which we had used, however, was found to contain some formic acid; nevertheless, the curve obtained, as in many other cases, fits in along with those for the other solvents. We had hoped to raise the rotation of nicotine into the neighbourhood of $[\alpha] = 0^\circ$ in order to be able to examine a definite region of anomalous dispersion, but we have found no "inert" solvent which is capable of producing this effect. It is one of the interesting things, however, about the study of optical activity in solution that a solvent which combines chemically with the active compound behaves in very much the same way as one which would normally be regarded as indifferent; otherwise the characteristic diagram would be impossible. The increase in the rotation of the nicotine in the experiment just mentioned was doubtless partly

due to the formamide itself and partly due to the action of the formic acid which it contained. Solution of nicotine in an excess * of 3·2095*N*-aqueous sulphuric acid raised the rotation at 0° to 30·45°, and, on heating, the rotation gradually fell to 19·5° at 90°.

From the data for the various solutions examined, the characteristic diagram shown in Fig. 2 is obtained. It will be seen that the data obtained lie in a fairly satisfactory manner on the lines of the diagram. The data for the rotation of nicotine in excess of sulphuric acid are in agreement with the others. It seems clear

FIG. 2.



Characteristic diagram of nicotine in ◎ *sulphuric acid (excess),* ⊙ *formamide,* ⊕ *water,* ⊕ *quinoline,* ✳ *o-nitrotoluene,* • *homogeneous.*

from the diagram that if the rotation for green light could be made to take on a value in the neighbourhood of + 3° or 4°, the rotation dispersion would be visibly anomalous; the lines of the characteristic diagram intersect over a range. The behaviour of nicotine may therefore be said to be normal, inasmuch as it conforms to that observed for the large majority of—if not indeed for all—active compounds.

When dispersion coefficients, $[\alpha]_{5790}/[\alpha]_{5461}$, are calculated for nicotine from these data using the rational zero + 3°, the values found show a very fair constancy, the mean value being 0·8674.

* Such that all the nicotine existed, presumably, as sulphate.

The colours of light used were as follows :

	r_1.	r_2.	y.	g.	b.	v.
λ	6716·3	6234·3	5790·3	5460·7	4959·7	4358·3

Homogeneous benzyl d-*dimethoxysuccinate.* Densities determined : 1·1730 at 16·4°; 1·1551 at 41°; 1·1320 at 70·75°; 1·1064 at 100°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·1813	72·83°	85·16°	100·6°	114·17°	148·6°	193·3°
16·3	1·1732	69·91	80·25	94·99	108·05	135·5	181·2
44·4	1·1523	62·29	73·42	86·14	98·54	123·8	166·1
70·5	1·1324	56·99	68·08	79·65	90·20	114·1	152·7
100	1·1064	52·40	61·64	72·72	82·84	104·0	139·8
139·5	1·0685	47·09	55·80	65·98	74·82	93·84	127·5
174·5	1·0321	43·31	51·45	60·32	68·58	86·21	117·6

Benzyl d-*dimethoxysuccinate in quinoline,* $p = 5{\cdot}1758$. Readings for some colours could not be taken at 100° owing to the darkening of the quinoline in solution. Densities determined : 1·0982 at 17·5°; 1·0740 at 48·5°; 1·0511 at 76°; 1·0312 at 100°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·1148	97·05°	114·3°	134·9°	154·6°	—	—
15·2	1·1020	90·64	105·3	126·6	142·9	178·8°	243·9°
44·2	1·0775	80·33	93·96	108·7	128·0	158·4	216·1
69·2	1·0566	72·97	84·30	100·4	115·0	142·0	198·8
100	1·0312	67·66	73·69	—	—	—	—

Benzyl d-*dimethoxysuccinate in nitrotoluene,* $p = 4{\cdot}860$. Densities determined : 1·1682 at 16·7°; 1·1413 at 43·4°; 1·1150 at 70·7°; 1·0874 at 100°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.
0°	1·1843	98·51°	115·2°	137·0°	155·5°	197·0°
13·6	1·1709	90·50	107·0	127·0	145·5	184·0
43·5	1·1411	79·13	93·2	109·0	124·2	158·4
72	1·1139	68·53	80·4	95·13	108·3	137·1
100	1·0874	61·12	71·2	83·45	95·8	119·0

Benzyl d-*dimethoxysuccinate in acetylene tetrabromide,* $p = 3{\cdot}066$. Densities determined : 2·8405 at 16·2°; 2·7853 at 42°; 2·7184 at 72·8°; 2·6651 at 98·8°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_v$.
0°	2·8755	47·18°	53·99°	63·18°	72·48°	118·2°
14·0	2·8452	45·40	53·73	62·25	70·62	116·2
44·2	2·7804	43·46	49·74	58·77	66·63	111·6
70·6	2·7238	40·59	47·42	55·92	63·34	105·4
98·8	2·6651	38·67	44·79	53·24	60·46	100·8

Benzyl d-*dimethoxysuccinate in* m-*xylene,* $p = 6{\cdot}6875$. Densities determined : 0·8865 at 14·2°; 0·8630 at 42·2°; 0·8375 at 71°; 0·8122 at 99°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
16·9°	0·8843	68·91°	77·68°	91·10°	103·5°	131·8°	175·3°
43·7	0·8614	60·22	70·31	83·11	95·04	120·7	160·0
69	0·8392	55·13	64·82	76·73	87·31	111·4	147·7
98·7	0·8126	50·47	59·58	70·39	80·28	102·4	135·4

d-*Dimethoxysuccinic acid in pyridine,* $p = 7{\cdot}8435$. Densities determined : 1·0137 at 15°; 0·9865 at 41·8°; 0·9621 at 66·7°; 0·9293 at 98·7°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·0287	129·9°	152·8°	181·0°	204·4°	255·3°	336·3°
14·8	1·0140	122·6	143·6	170·1	192·0	241·2	318·9
46·4	0·9819	111·4	130·1	151·3	172·6	218·0	287·8
69	0·9592	103·1	120·2	142·4	161·2	201·1	268·4
99	0·9293	92·8	110·0	128·2	146·1	184·0	243·5

d-*Dimethoxysuccinic acid in acetone*, $p = 15{\cdot}982$. Densities determined: 0·8558 at 21·5°; 0·8433 at 33°; 0·8327 at 42·8°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.
0°	0·8787	70·08°	81·82°	95·36°	108·5°
12	0·8656	70·24	80·08	94·00	106·3
30·5	0·8459	68·15	76·52	91·96	103·8
46·6	0·8283	65·95	73·12	88·98	100·8

Methyl d-*dimethoxysuccinate in quinoline*, $p = 5{\cdot}502$. Densities determined: 1·1026 at 14°; 1·0804 at 40·7°; 1·0582 at 68·3°; 1·0326 at 100·2°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_v$.
0°	1·1138	84·04°	97·74°	114·6°	129·4°	211·5°
13·5	1·1030	83·54	97·05	114·0	129·4	211·7
36·3	1·0844	81·79	94·69	111·0	125·9	208·5
67	1·0595	77·36	88·51	105·7	119·4	198·0
99·6	1·0332	—	80·92	98·2	110·8	unreadable

Benzyl tartrate in quinoline, $p = 9{\cdot}4489$. Densities determined: 1·1080 at 17°; 1·0878 at 40·2; 1·0627 at 72°; 1·0408 at 98·9°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.
0°	1·1213	31·34°	37·79°	43·56°	48·88°
13·5	1·1103	29·92	34·60	40·51	45·58
48·8	1·0818	25·26	30·46	34·89	38·63
74·2	1·0610	21·95	27·73	31·69	34·86
98·9	1·0408	21·57	25·04	30·29	32·15

Nicotine in formamide solution. The formamide contained some formic acid and caused a rise in rotation in the absolute sense from that obtained with pure formamide, $p = 18{\cdot}5040$. Densities determined: 1·1328 at 14·9°; 1·1061 at 50·8°; 1·0877 at 73·7°; 1·0660 at 99·3°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·1433	−20·99°	−25·57°	−30·77°	−36·30°	−49·35°	−73·88°
16·0	1·1325	26·01	30·97	37·36	43·66	58·89	86·99
44·6	1·1103	33·29	39·52	47·16	55·15	73·25	106·0
70·4	1·0899	39·82	47·90	56·72	66·25	87·12	124·8
99	1·0665	47·68	56·50	66·43	76·87	102·1	144·1

Solution of nicotine in o-*nitrotoluene*, $p = 4{\cdot}7337$. Densities determined: 1·1582 at 15·7°; 1·1322 at 43°; 1·1024 at 75°; 1·0789 at 99°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.
0°	1·1733	−128·4°	−153·7°	−184·1°	−211·0°	−277·3°
14·1	1·1598	129·4	154·5	182·1	211·0	278·3
40·8	1·1346	130·7	154·3	182·7	211·1	277·2
74·4	1·1025	130·6	154·7	182·6	211·4	277·6
99·2	1·0878	129·9	153·9	182·2	210·4	—

Solution of nicotine in quinoline, $p = 9{\cdot}1365$. Densities determined: 1·0888 at 15·3°; 1·0626 at 48·9°; 1·0413 at 75·2°; 1·0217 at 99·4°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·1010	−93·75°	−110·3°	−131·3°	−151·3°	−197·2°	−274·9°
17	1·0878	96·59	114·8	137·1	158·1	205·4	287·1
43·7	1·0665	102·4	121·0	144·5	166·5	216·9	302·8
80	1·0375	107·4	127·2	151·6	174·9	227·8	317·6
99·2	1·0220	109·4	129·7	154·5	178·3	226·6	324·2

Nicotine in α-bromonaphthalene. Some naphthalene was also present as impurity. No rotations could be observed at 0° owing to partial solidification of the mixture, $p = 4{\cdot}3213$. Densities determined: 1·4668 at 10·7°; 1·4335 at 45·2°; 1·4081 at 70·4°; 1·3788 at 100°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
12·6°	1·4650	−111·4°	−133·6°	−163·5°	−188·9°	−241·2°	−337·9°
41·1	1·4367	117·1	139·0	166·7	191·4	244·7	342·3
69·6	1·4085	119·9	140·3	168·1	192·6	252·2	345·9
99·2	1·3800	121·1	141·0	167·4	194·5	254·1	343·8

Homogeneous nicotine. Densities determined: 1·0124 at 14·8°; 0·99037 at 41·0°; 0·9688 at 70°; 0·9449 at 99·2°.

t.	*d.*	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_v$.
0°	1·0212	−175·6°	−202·8°	−371·2°
14·2	1·0108	176·4	204·2	372·8
39	0·9925	177·9	206·0	376·1
71·5	0·9673	179·3	207·1	377·0
99	0·9453	179·7	207·2	377·1

Nicotine in ethyl acetate. The rotation values for the highest temperature show a sudden rise in the absolute sense; this may be due in part to loss of solvent at that temperature, $p = 10{\cdot}701$. Densities determined: 0·9143 at 15°; 0·8893 at 37·7°; 0·8569 at 64·7°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	0·9294	−127·7°	−151·0°	−180·7°	−208·2°	−268·8°	−376·8°
15·2	0·9135	129·0	152·1	181·0	209·4	269·1	378·2
40·8	0·8855	127·0	153·7	182·6	210·5	274·0	380·9
60	0·8626	116·2	141·3	171·0	198·1	253·2	355·9

Nicotine in water, $p = 9{\cdot}3930$. Densities determined: 1·0060 at 15·1°; 1·0003 at 32·8°; 0·9912 at 52·6°; 0·9820 at 68·5°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·0098	−54·57°	−64·68°	−77·15°	−90·25°	−119·0°	−170·0°
24·5	1·0031	58·74	70·15	83·41	97·22	127·5	182·4
47·5	0·9935	63·07	75·40	89·69	104·4	137·3	194·7
67·6	0·9827	68·08	80·18	95·63	111·1	144·7	205·4

Nicotine in excess of sulphuric acid. To 3·5241 g. of nicotine were added 24 c.c. of 3·2095*N*-H_2SO_4, $p = 11{\cdot}880$. Densities determined: 1·1085 at 13·8°; 1·0920 at 46·8°; 1·0798 at 67°; 1·0645 at 90°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·1145	+22·10°	+25·63°	+30·30°	+34·46°	+43·43°	+58·06°
26·6	1·1027	18·46	21·56	25·48	29·39	37·45	49·61
44·8	1·0931	16·41	19·30	22·86	26·23	33·06	44·56
66·8	1·0800	14·37	16·76	20·02	22·70	28·74	38·58
90	1·0645	12·16	14·33	17·05	19·42	24·56	32·86

We are indebted to the Carnegie Trustees for the Universities of Scotland for a scholarship, and for grants which have defrayed much of the expense of this investigation.

UNIVERSITY OF GLASGOW. [*Received, July 6th,* 1925.]

CCCXXXII.—p-*Dimethylaminodiphenylacetic Acid.*

By DALIP SINGH.

VORLÄNDER and SIEBERT have shown (*Ber.*, 1906, **39**, 1024) that barium diphenylacetate on distillation gives, together with other products, tetraphenylallene. The preparation of p-*dimethylaminodiphenylacetic acid* (III) was therefore undertaken, for should its barium salt (I) decompose in like manner, the product, tetramethyldiaminotetraphenylallene (II), would furnish a suitable material for testing van 't Hoff's view of the molecular asymmetry of compounds of the substituted allene type.

$$\underset{\text{(I.)}}{\left(\begin{matrix}NMe_2\cdot C_6H_4\\ Ph\end{matrix}\!>\!CH\cdot CO_2\right)_2Ba} \longrightarrow \underset{\text{(II.)}}{\begin{matrix}NMe_2\cdot C_6H_4\\ Ph\end{matrix}\!>\!C{:}C{:}C\!<\!\begin{matrix}C_6H_4\cdot NMe_2\\ Ph\end{matrix}}$$

The desired synthesis was effected by hydrolysing *ethyl* p-*dimethylaminobenzilate* (V), prepared by the action of *p*-dimethylaminophenylglyoxylic ester (IV) (Guyot, *Compt. rend.*, 1907, **144**, 1120) on magnesium phenyl bromide, to the corresponding *acid* (VI) and reducing the latter with hydriodic acid and phosphorus.

$$\underset{\text{(IV.)}}{NMe_2\cdot C_6H_4\cdot CO\cdot CO_2Et} \longrightarrow \underset{\text{(V.)}}{NMe_2\cdot C_6H_4\cdot CPh(OH)\cdot CO_2Et} \longrightarrow \underset{\text{(VI.)}}{NMe_2\cdot C_6H_4\cdot CPh(OH)\cdot CO_2H} \longrightarrow \underset{\text{(III.)}}{NMe_2\cdot C_6H_4\cdot CHPh\cdot CO_2H}$$

Difficulties, eventually overcome, were encountered in the Grignard reaction. The reagent readily attacked the dimethylamino-group and the whole of the ester was precipitated in the form of a compound. (This, on decomposition with water, regenerated the original ester and therefore probably had the constitution $MgPh\cdot NMe_2Br\cdot C_6H_4\cdot CO\cdot CO_2Et$; compare Kauffmann, *Ber.*, 1913, **46**, 2929.) Moreover, the use of too great an excess of the Grignard reagent had to be avoided, otherwise the carbethoxy-group of the ester also was attacked and the *glycol*

$$NMe_2\cdot C_6H_4\cdot CPh(OH)\cdot CPh_2\cdot OH \text{ (VII)}$$

produced.

The best results in the desired direction were achieved by adding an ethereal solution of the ester (IV) to the Grignard reagent (2·5 mols.) and working up the product immediately.

The behaviour of barium, calcium, and lead *p*-dimethylaminodiphenylacetates on dry distillation was investigated. The dry salt was distilled in a high vacuum in a specially designed apparatus. From the barium salt an oil was obtained, from which a crystalline solid, having the composition of *di*-p-*dimethylaminobenzhydryl ketone*, $CO(CHPh\cdot C_6H_4\cdot NMe_2)_2$ (VIII), and *p*-dimethylaminodiphenylmethane were isolated, but none of the allene derivative (III). Now, although Vorländer and Siebert obtained a considerable

quantity of diphenylmethane together with tetraphenylallene by distilling barium diphenylacetate, they were unable to detect any dibenzhydryl ketone. It would appear, therefore, that the presence of the tertiary amino-group in dimethylaminodiphenylacetic acid favours the formation of the ketone and prevents that of the allene.

The preparation of *ethyl phenyl-4-pyridylpyruvate*,

$$C_5NH_4{\cdot}CHPh{\cdot}CO{\cdot}CO_2Et \text{ (IX)},$$

was next undertaken. This compound is a possible source of phenylpyridylacetic acid, from which a substituted allene of the desired type might be obtained. The ester was synthesised by condensing 4-benzylpyridine and ethyl oxalate with potassium ethoxide (compare Wislicenus, *Ber.*, 1909, **42**, 1140). The acid produced by hydrolysing the ester was unstable and difficult to purify. Its sodium salt was oxidised by hydrogen peroxide with formation of sodium phenylpyridylacetate. The acid liberated from this immediately decomposed into benzylpyridine and carbon dioxide.

Corresponding condensations of benzylpyridine with other esters such as ethyl benzoate, ethyl formate, and ethyl carbonate could not be carried out.

EXPERIMENTAL.

Ethyl p-*Dimethylaminobenzilate* (V).—To a well-cooled ethereal solution of the Grignard reagent prepared from magnesium (3 g.) and bromobenzene (19·5 g.) is gradually added an ethereal solution of ethyl *p*-dimethylaminophenylglyoxylate (11 g.), and the reaction mixture is immediately poured on to a mixture of ice and dilute hydrochloric acid. The aqueous layer is treated with ammonium chloride and ammonia and extracted with ether. From the washed extract, dried with potassium carbonate, an oil is obtained which changes to a pasty solid on scratching; this is filtered off and crystallised from absolute alcohol. The *ester* thus obtained (yield 9 g.) melts at 96—97° (Found : C, 72·1 ; H, 7·1 ; N, 4·5. $C_{18}H_{21}O_3N$ requires C, 72·2 ; H, 7·0 ; N, 4·7%). It is very soluble in chloroform, benzene, or acetone, less soluble in ethyl or methyl alcohol, or ether, sparingly soluble in petroleum, and insoluble in water.

p-*Dimethylaminotetraphenylethylene glycol* (VII) is obtained as a by-product of the preceding reaction when too great an excess of the Grignard reagent has been used. The yield increases considerably if the reaction mixture is kept for a long time before being decomposed; and on heating, the *glycol* is almost the sole product. It is worked up in the same manner as the hydroxy-ester. It separates from much boiling alcohol in glistening crystals, m. p. 193—194° (Found : C, 82·2 ; H, 6·4 ; N, 3·3. $C_{28}H_{27}O_2N$ requires C, 82·1 ; H, 6·6 ; N, 3·4%), which are soluble in benzene,

acetone, chloroform or acetic acid, and sparingly soluble in ethyl or methyl alcohol, or ether.

p-*Dimethylaminobenzilic Acid* (VI).—The ester (V) is heated under reflux with a slight excess of alcoholic sodium hydroxide for 4 hours, the alcohol evaporated, and the alkaline solution, after being shaken with ether to remove unchanged material, exactly neutralised with dilute sulphuric acid. The *acid*, isolated by means of ether, is obtained as a crystalline solid, m. p. 50—55°, after drying in a vacuum desiccator (Found : C, 69·5; H, 6·5. $C_{16}H_{17}O_3N$ requires C, 70·8; H, 6·3%). It is unstable, becoming yellow and finally green on keeping, and yellow on warming. It is very soluble in most of the organic solvents, except light petroleum, but is recovered from the solutions in a viscous condition.

p-*Dimethylaminodiphenylacetic Acid* (III).—The sodium salt of the hydroxy-acid (10 g.; obtained by evaporating an alkaline solution prepared as described above) is gently boiled under reflux with red phosphorus (5 g.) and constant-boiling hydriodic acid (50 c.c.) for about 6 hours. The diluted, filtered solution deposits, on cooling, colourless crystals of the hydriodide of *p*-dimethylaminodiphenylacetic acid. This, after being washed with a little water, is exactly neutralised, in aqueous solution, with ammonia, methyl-orange being used as indicator. The *acid* is then extracted with ether, and crystallised from hot alcohol, separating in silky, white needles, m. p. 104—105° (Found : C, 75·5; H, 6·8; N, 5·3. $C_{16}H_{17}O_2N$ requires C, 75·3; H, 6·7; N, 5·5%). It dissolves readily in chloroform, acetone, or benzene, less readily in ethyl or methyl alcohol or ether, and is sparingly soluble in light petroleum.

Di-p-*dimethylaminobenzhydryl Ketone* (VIII).—In a glass tube, sealed at one end and provided with an air-tight glass stopper at the other, is placed a cylindrical copper vessel filled with 2 g. of barium *p*-dimethylaminodiphenylacetate, thoroughly dried at 150—160°. The tube is connected by means of a side tube with a charcoal–liquid air vacuum apparatus, which can communicate by a three-way tap with a Fleuss pump or with the atmosphere. The whole apparatus is evacuated first with the pump and then by means of the charcoal cooled in liquid air. Heating is effected by a metal bath, and the distillation is continued so long as reddish-brown oil collects in a bulb blown in the tube near its sealed end.

The oil is washed with acetone. The washings slowly deposit a white solid, which crystallises from much boiling alcohol in thin needles, m. p. 190° (Found : C, 83·5, 83·3; H, 7·2, 7·1. $C_{31}H_{32}ON_2$ requires C, 83·0; H, 7·1%). The *ketone* dissolves readily in chloroform or carbon disulphide, is fairly easily soluble in ether or petroleum, less soluble in benzene or acetone, and very sparingly soluble in

ethyl or methyl alcohol. Its behaviour towards ketonic reagents was not examined, as the less complex dibenzhydryl ketone was known to be inert towards hydroxylamine, phenylhydrazine, and semicarbazide (Vorländer and Rack, *Ber.*, 1923, **56**, 1126).

The oil remaining after the ketone has been removed is fractionally distilled; the greenish-brown oil that passes over at 175°/2—3 mm. solidifies when cooled and scratched. By crystallising it from petroleum, *p*-dimethylaminodiphenylmethane (Limpricht, *Annalen*, 1899, **307**, 310) is obtained in thin leaflets, m. p. 31° (Found: C, 85·6; H, 8·0. Calc., C, 85·3; H, 8·0%).

Ethyl Phenyl-4-pyridylpyruvate (IX).—To a solution of potassium ethoxide (1 g. potassium) in 4 g. of alcohol are added in turn ether (20—30 c.c.), ethyl oxalate (3·8 g.), and 4-benzylpyridine (4·3 g.; 1 mol.). After 12 hours, the yellow potassium salt that has been deposited is decomposed by a slight excess of glacial acetic acid, ice-water added, and the ester together with the uncondensed material extracted with ether. From the washed and dried extract a solid is obtained which separates from alcohol in glistening, yellow crystals, melting at 123—124° to a yellowish-green liquid (yield about 33%) (Found: C, 71·3; H, 5·7; N, 5·4. $C_{16}H_{15}O_3N$ requires C, 71·4; H, 5·6; N, 5·2%). The *ester* is fairly easily soluble in benzene, chloroform, or acetone, less soluble in ethyl or methyl alcohol, sparingly soluble in ether, and insoluble in light petroleum.

The ester is left over-night in a cold dilute alcoholic solution of sodium hydroxide, water is then added, and the unchanged material removed with ether. The alkaline solution is acidified with acetic acid and shaken with chloroform. The chloroform in the extract is evaporated in a current of air, and the residue is freed from acetic acid by soda-lime in a desiccator. *Phenyl-4-pyridylpyruvic acid* is thus obtained as a yellow oil which solidifies when rubbed with benzene or crystallised from alcohol. It turns green at 100° and melts indefinitely at 110° (Found: C, 72·7; H, 5·2; N, 6·1. $C_{14}H_{11}O_3N$ requires C, 69·7; H, 4·6; N, 5·8%). The acid is very soluble in alcohol, acetic acid, or acetone, less soluble in benzene, and very sparingly soluble in light petroleum.

Phenylpyridylpyruvic acid oxime hydrochloride is obtained by mixing equivalent quantities of hydroxylamine hydrochloride and sodium phenylpyridylpyruvate in aqueous solution; crystals, m. p. 52—53°, of the *hydrochloride* are deposited after 12 hours (Found: C, 57·4; H, 4·3. $C_{14}H_{12}O_3N_2,HCl$ requires C, 57·4; H, 4·4%).

Sodium Phenyl-4-pyridylacetate.—On addition of the calculated quantity of hydrogen peroxide (30%) to an aqueous solution of

sodium phenylpyridylpyruvate, there is a rapid evolution of gas; the colour is completely discharged in about 1 hour. The solution of the sodium salt thus obtained, on being acidified, gives some 4-benzylpyridine, which is probably produced by decomposition of phenylpyridylacetic acid.

2-α-4-*Pyridylbenzyl*-3-*quinoxalone*, $C_6H_4<\begin{matrix}N=C\cdot CHPh\cdot C_5NH_4\\ NH\cdot CO\end{matrix}$.—Alcoholic solutions of equimolecular quantities of ethyl phenyl-4-pyridylpyruvate and *o*-phenylenediamine are heated together on a water-bath for 2 hours; the solid that separates is washed, and crystallised from hot pyridine; m. p. 294—295° (Found: C, 76·7; H, 4·8; N, 13·0. $C_{20}H_{15}ON_3$ requires C, 76·7; H, 4·8; N, 13·4%).

This work was carried out under the supervision of Dr. W. H. Mills, F.R.S., and the author is indebted to Prof. Sir William Pope for providing facilities in the laboratory.

University Chemical Laboratory,
Cambridge. [*Received, July 30th*, 1925.]

NOTES.

Selenium as a Chlorine Carrier. By Oswald Silberrad and Charles A. Silberrad.

The observations (Silberrad, C. A. Silberrad, and Parke, this vol., p. 1724) that selenium acted as a catalyst towards sulphuryl chloride in a perfectly normal manner, *i.e.*, midway between tellurium and sulphur, and that the catalysts examined appeared to behave as chlorine carriers rather than as dissociation catalysts made it of interest to reinvestigate Willgerodt's work (*J. pr. Chem.*, 1885, **31**, 539; 1888, **34**, 264) on direct chlorination, which led him to the conclusion that selenium does not act, in that case, as a chlorine carrier at all.

To this end dual experiments were conducted. Chlorine (1 mol.) was passed into boiling toluene (1) without and (2) with the addition of selenium chloride; each experiment was repeated (*a*) in total darkness and (*b*) in an apparatus so arranged that the vapour was exposed to light; the quantities of chlorotoluene and benzyl chloride produced were determined as recently described (*loc. cit.*). The results were as follows:

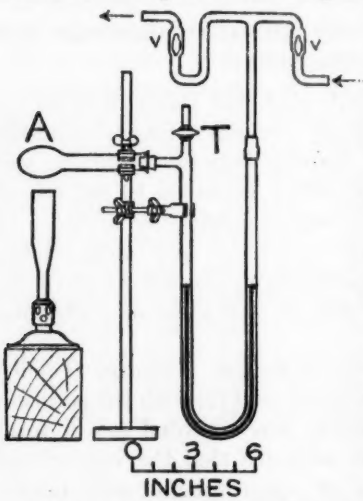
Conditions of expt.	$d_{4^\circ}^{15^\circ}$.	Composition of product %. Chlorine.	Toluene.	Chlorotoluene.	Benzyl chloride.	Ratio Chlorotoluene/benzyl chloride.
(*a*) In total darkness.						
No catalyst	0·961	12·4	55·8	2·7	41·5	0·065
With selenium (1·0 g. of $SeCl_4$)*	0·983	15·8	43·4	33·7	22·9	1·472
(*b*) Vapour exposed to light.						
No catalyst	0·988	16·2	42·3	10·6	47·1	0·225
With selenium (0·3 g. of $SeCl_4$)*	1·004	18·3	34·6	29·5	35·9	0·82

* The selenium chloride was prepared by passing dry chlorine over the element, with which, contrary to the literature (Sacc, *Ann. Chim. Phys.*, 1848, **23**, 124), both varieties react at the ordinary temperature, passing through the mono- to the tetra-chloride.

From these results it is evident that, contrary to the literature, selenium does act as a carrier in direct chlorination; its presence not only raises the ratio of nuclear to side-chain substitution, but also, to a lesser extent, increases the amount of chlorine which enters into combination in a given time.—THE SILBERRAD RESEARCH LABORATORIES, BUCKHURST HILL, ESSEX. [*Received, August 11th*, 1925.]

A Simple Form of Gas Circulating Apparatus. By A. R. PEARSON and J. S. G. THOMAS.

FOR circulating a volume of gas through a closed system, apparatus depending on the force-pump principle has been described by Bone and Sarjant (*Proc. Roy. Soc.*, 1919, **96**, *A*, 126) and by Davis, Place, and Edeburn (*Fuel*, 1925, **4**, 290); in each case the piston is mercury contained in a U-tube.



A prime mover for the mercury–U-tube type of circulating pump can be made very simply from ordinary laboratory apparatus, utilising the principle of the hot-air engine (see Griffiths, "The Thermal Measurement of Energy," 1901, p. 50). The complete apparatus is shown in the figure. The bulb A is heated by a burner, and when a pressure difference of two or three inches is indicated by the U-tube the mercury is set in oscillation by quickly opening

and closing the tap, T, in such a way that the pressure in the hot bulb is suddenly reduced as nearly as possible to equality with that on the other side of the U-tube. The mercury will then continue to oscillate as long as heat is supplied to the bulb, and by the operation of the glass valves, V, or other suitable valves, gas can be forced through the system in the direction of the arrows. To ensure regularity of operation, suitable dimensions must be chosen for the mercury column and the hot bulb. With the dimensions shown, the apparatus drives about 2 cubic feet of gas per hour against a total back pressure of about 3 inches of water.—South Metropolitan Gas Co., London, S.E. 15. [*Received, July 15th*, 1925.]

The Action of Metals on Dipentene Dihydrohalide. Preparation of a Synthetic Diterpene. By Kenneth Charles Roberts.

Alcoholic solutions of *cis-* and *trans*-dipentene dihydrobromide and of *trans*-dipentene dihydrochloride were each shaken at room temperature with molecular silver until reaction was complete, this being indicated when no precipitate was formed on dilution of a portion of the reaction mixture with water. The action of finely-divided copper was tried in the same way. (The action of sodium was investigated by Montgolfier, *Ann. Chim. Phys.*, 1880, **19**, 155). In no case was metal halide formed. There was therefore no condensation, but simply loss of halogen acid and production of dipentene. This polymerised to a diterpene, which was isolated as a colourless, highly viscous liquid with a faint terpene-like odour, b. p. 173—183°/13 mm., $n_D^{20°}$ 1·5170, $d^{20°}$ 0·9361 (Found: C, 88·4; H, 12·0; *M*, 273, 266; iodine value, 103. $C_{20}H_{32}$ requires C, 88·2; H, 11·8%; *M*, 272; iodine value, for one double linking, 94). β-Camphorene has b. p. 170—180°/10 mm., n_D 1·5180, and $d^{20°}$ 0·9300 (Semmler and Rosenberg, *Ber.*, 1913, **46**, 768).—University of Otago, New Zealand. [*Received, August 11th*, 1925.]

Conditions of expt.	$d_4^{16°}$.	Composition of product %. Chlorine.	Toluene.	Chlorotoluene.	Benzyl chloride.	Ratio Chlorotoluene/benzyl chloride.
		(*a*) In total darkness.				
No catalyst	0·961	12·4	55·8	2·7	41·5	0·065
With selenium (1·0 g. of $SeCl_4$)*	0·983	15·8	43·4	33·7	22·9	1·472
		(*b*) Vapour exposed to light.				
No catalyst	0·988	16·2	42·3	10·6	47·1	0·225
With selenium (0·3 g. of $SeCl_4$)*	1·004	18·3	34·6	29·5	35·9	0·82

* The selenium chloride was prepared by passing dry chlorine over the element, with which, contrary to the literature (Sacc, *Ann. Chim. Phys.*, 1848, **23**, 124), both varieties react at the ordinary temperature, passing through the mono- to the tetra-chloride.

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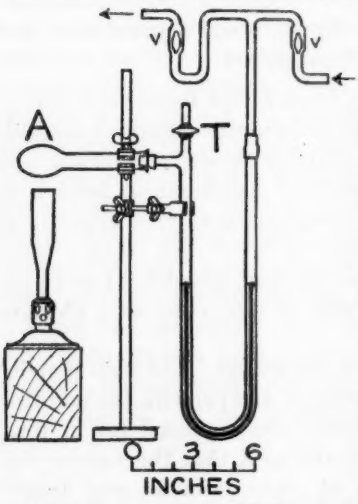

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Nicotine in α-bromonaphthalene. Some naphthalene was also present as impurity. No rotations could be observed at 0° owing to partial solidification of the mixture, $p = 4{\cdot}3213$. Densities determined: 1·4668 at 10·7°; 1·4335 at 45·2°; 1·4081 at 70·4°; 1·3788 at 100°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
12·6°	1·4650	−111·4°	−133·6°	−163·5°	−188·9°	−241·2°	−337·9°
41·1	1·4367	117·1	139·0	166·7	191·4	244·7	342·3
69·6	1·4085	119·9	140·3	168·1	192·6	252·2	345·9
99·2	1·3800	121·1	141·0	167·4	194·5	254·1	343·8

Homogeneous nicotine. Densities determined: 1·0124 at 14·8°; 0·99037 at 41·0°; 0·9688 at 70°; 0·9449 at 99·2°.

t.	*d.*	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_v$.
0°	1·0212	−175·6°	−202·8°	−371·2°
14·2	1·0108	176·4	204·2	372·8
39	0·9925	177·9	206·0	376·1
71·5	0·9673	179·3	207·1	377·0
99	0·9453	179·7	207·2	377·1

Nicotine in ethyl acetate. The rotation values for the highest temperature show a sudden rise in the absolute sense; this may be due in part to loss of solvent at that temperature, $p = 10{\cdot}701$. Densities determined: 0·9143 at 15°; 0·8893 at 37·7°; 0·8569 at 64·7°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	0·9294	−127·7°	−151·0°	−180·7°	−208·2°	−268·8°	−376·8°
15·2	0·9135	129·0	152·1	181·0	209·4	269·1	378·2
40·8	0·8855	127·0	153·7	182·6	210·5	274·0	380·9
60	0·8626	116·2	141·3	171·0	198·1	253·2	355·9

Nicotine in water, $p = 9{\cdot}3930$. Densities determined: 1·0060 at 15·1°; 1·0003 at 32·8°; 0·9912 at 52·6°; 0·9820 at 68·5°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·0098	−54·57°	−64·68°	−77·15°	−90·25°	−119·0°	−170·0°
24·5	1·0031	58·74	70·15	83·41	97·22	127·5	182·4
47·5	0·9935	63·07	75·40	89·69	104·4	137·3	194·7
67·6	0·9827	68·08	80·18	95·63	111·1	144·7	205·4

Nicotine in excess of sulphuric acid. To 3·5241 g. of nicotine were added 24 c.c. of 3·2095*N*-H_2SO_4, $p = 11{\cdot}880$. Densities determined: 1·1085 at 13·8°; 1·0920 at 46·8°; 1·0798 at 67°; 1·0645 at 90°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·1145	+22·10°	+25·63°	+30·30°	+34·46°	+43·43°	+58·06°
26·6	1·1027	18·46	21·56	25·48	29·39	37·45	49·61
44·8	1·0931	16·41	19·30	22·86	26·23	33·06	44·56
66·8	1·0800	14·37	16·76	20·02	22·70	28·74	38·58
90	1·0645	12·16	14·33	17·05	19·42	24·56	32·86

We are indebted to the Carnegie Trustees for the Universities of Scotland for a scholarship, and for grants which have defrayed much of the expense of this investigation.

UNIVERSITY OF GLASGOW. [*Received, July 6th,* 1925.]

CCCXXXII.—p-*Dimethylaminodiphenylacetic Acid.*

By DALIP SINGH.

VORLÄNDER and SIEBERT have shown (*Ber.*, 1906, **39**, 1024) that barium diphenylacetate on distillation gives, together with other products, tetraphenylallene. The preparation of p-*dimethylaminodiphenylacetic acid* (III) was therefore undertaken, for should its barium salt (I) decompose in like manner, the product, tetramethyldiaminotetraphenylallene (II), would furnish a suitable material for testing van 't Hoff's view of the molecular asymmetry of compounds of the substituted allene type.

$$\underset{\text{(I.)}}{\left(\begin{matrix}NMe_2\cdot C_6H_4\\ Ph\end{matrix}\!\!>\!CH\cdot CO_2\right)_2}Ba \longrightarrow \begin{matrix}NMe_2\cdot C_6H_4\\ Ph\end{matrix}\!\!>\!C\!:\!C\!:\!C\!<\!\!\begin{matrix}C_6H_4\cdot NMe_2\\ Ph\end{matrix}\quad \underset{\text{(II.)}}{}$$

The desired synthesis was effected by hydrolysing *ethyl* p-*dimethylaminobenzilate* (V), prepared by the action of *p*-dimethylaminophenylglyoxylic ester (IV) (Guyot, *Compt. rend.*, 1907, **144**, 1120) on magnesium phenyl bromide, to the corresponding *acid* (VI) and reducing the latter with hydriodic acid and phosphorus.

$$\text{(IV.)}\ NMe_2\cdot C_6H_4\cdot CO\cdot CO_2Et \longrightarrow NMe_2\cdot C_6H_4\cdot CPh(OH)\cdot CO_2Et\ \text{(V.)}$$
$$\longrightarrow NMe_2\cdot C_6H_4\cdot CPh(OH)\cdot CO_2H\ \overline{\text{(VI.)}} \longrightarrow NMe_2\cdot C_6H_4\cdot CHPh\cdot CO_2H\ \text{(III.)}$$

Difficulties, eventually overcome, were encountered in the Grignard reaction. The reagent readily attacked the dimethylamino-group and the whole of the ester was precipitated in the form of a compound. (This, on decomposition with water, regenerated the original ester and therefore probably had the constitution $MgPh\cdot NMe_2Br\cdot C_6H_4\cdot CO\cdot CO_2Et$; compare Kauffmann, *Ber.*, 1913, **46**, 2929.) Moreover, the use of too great an excess of the Grignard reagent had to be avoided, otherwise the carbethoxy-group of the ester also was attacked and the *glycol*

$$NMe_2\cdot C_6H_4\cdot CPh(OH)\cdot CPh_2\cdot OH\ \text{(VII)}$$

produced.

The best results in the desired direction were achieved by adding an ethereal solution of the ester (IV) to the Grignard reagent (2·5 mols.) and working up the product immediately.

The behaviour of barium, calcium, and lead *p*-dimethylaminodiphenylacetates on dry distillation was investigated. The dry salt was distilled in a high vacuum in a specially designed apparatus. From the barium salt an oil was obtained, from which a crystalline solid, having the composition of *di*-p-*dimethylaminobenzhydryl ketone*, $CO(CHPh\cdot C_6H_4\cdot NMe_2)_2$ (VIII), and *p*-dimethylaminodiphenylmethane were isolated, but none of the allene derivative (III). Now, although Vorländer and Siebert obtained a considerable

quantity of diphenylmethane together with tetraphenylallene by distilling barium diphenylacetate, they were unable to detect any dibenzhydryl ketone. It would appear, therefore, that the presence of the tertiary amino-group in dimethylaminodiphenylacetic acid favours the formation of the ketone and prevents that of the allene.

The preparation of *ethyl phenyl-4-pyridylpyruvate*,

$$C_5NH_4\cdot CHPh\cdot CO\cdot CO_2Et \text{ (IX)},$$

was next undertaken. This compound is a possible source of phenylpyridylacetic acid, from which a substituted allene of the desired type might be obtained. The ester was synthesised by condensing 4-benzylpyridine and ethyl oxalate with potassium ethoxide (compare Wislicenus, *Ber.*, 1909, **42**, 1140). The acid produced by hydrolysing the ester was unstable and difficult to purify. Its sodium salt was oxidised by hydrogen peroxide with formation of sodium phenylpyridylacetate. The acid liberated from this immediately decomposed into benzylpyridine and carbon dioxide.

Corresponding condensations of benzylpyridine with other esters such as ethyl benzoate, ethyl formate, and ethyl carbonate could not be carried out.

Experimental.

Ethyl p-*Dimethylaminobenzilate* (V).—To a well-cooled ethereal solution of the Grignard reagent prepared from magnesium (3 g.) and bromobenzene (19·5 g.) is gradually added an ethereal solution of ethyl *p*-dimethylaminophenylglyoxylate (11 g.), and the reaction mixture is immediately poured on to a mixture of ice and dilute hydrochloric acid. The aqueous layer is treated with ammonium chloride and ammonia and extracted with ether. From the washed extract, dried with potassium carbonate, an oil is obtained which changes to a pasty solid on scratching; this is filtered off and crystallised from absolute alcohol. The *ester* thus obtained (yield 9 g.) melts at 96—97° (Found: C, 72·1; H, 7·1; N, 4·5. $C_{18}H_{21}O_3N$ requires C, 72·2; H, 7·0; N, 4·7%). It is very soluble in chloroform, benzene, or acetone, less soluble in ethyl or methyl alcohol, or ether, sparingly soluble in petroleum, and insoluble in water.

p-*Dimethylaminotetraphenylethylene glycol* (VII) is obtained as a by-product of the preceding reaction when too great an excess of the Grignard reagent has been used. The yield increases considerably if the reaction mixture is kept for a long time before being decomposed; and on heating, the *glycol* is almost the sole product. It is worked up in the same manner as the hydroxy-ester. It separates from much boiling alcohol in glistening crystals, m. p. 193—194° (Found: C, 82·2; H, 6·4; N, 3·3. $C_{28}H_{27}O_2N$ requires C, 82·1; H, 6·6; N, 3·4%), which are soluble in benzene,

acetone, chloroform or acetic acid, and sparingly soluble in ethyl or methyl alcohol, or ether.

p-*Dimethylaminobenzilic Acid* (VI).—The ester (V) is heated under reflux with a slight excess of alcoholic sodium hydroxide for 4 hours, the alcohol evaporated, and the alkaline solution, after being shaken with ether to remove unchanged material, exactly neutralised with dilute sulphuric acid. The *acid*, isolated by means of ether, is obtained as a crystalline solid, m. p. 50—55°, after drying in a vacuum desiccator (Found : C, 69·5; H, 6·5. $C_{16}H_{17}O_3N$ requires C, 70·8; H, 6·3%). It is unstable, becoming yellow and finally green on keeping, and yellow on warming. It is very soluble in most of the organic solvents, except light petroleum, but is recovered from the solutions in a viscous condition.

p-*Dimethylaminodiphenylacetic Acid* (III).—The sodium salt of the hydroxy-acid (10 g.; obtained by evaporating an alkaline solution prepared as described above) is gently boiled under reflux with red phosphorus (5 g.) and constant-boiling hydriodic acid (50 c.c.) for about 6 hours. The diluted, filtered solution deposits, on cooling, colourless crystals of the hydriodide of *p*-dimethylaminodiphenylacetic acid. This, after being washed with a little water, is exactly neutralised, in aqueous solution, with ammonia, methyl-orange being used as indicator. The *acid* is then extracted with ether, and crystallised from hot alcohol, separating in silky, white needles, m. p. 104—105° (Found : C, 75·5; H, 6·8; N, 5·3. $C_{16}H_{17}O_2N$ requires C, 75·3; H, 6·7; N, 5·5%). It dissolves readily in chloroform, acetone, or benzene, less readily in ethyl or methyl alcohol or ether, and is sparingly soluble in light petroleum.

Di-p-*dimethylaminobenzhydryl Ketone* (VIII).—In a glass tube, sealed at one end and provided with an air-tight glass stopper at the other, is placed a cylindrical copper vessel filled with 2 g. of barium *p*-dimethylaminodiphenylacetate, thoroughly dried at 150—160°. The tube is connected by means of a side tube with a charcoal–liquid air vacuum apparatus, which can communicate by a three-way tap with a Fleuss pump or with the atmosphere. The whole apparatus is evacuated first with the pump and then by means of the charcoal cooled in liquid air. Heating is effected by a metal bath, and the distillation is continued so long as reddish-brown oil collects in a bulb blown in the tube near its sealed end.

The oil is washed with acetone. The washings slowly deposit a white solid, which crystallises from much boiling alcohol in thin needles, m. p. 190° (Found : C, 83·5, 83·3; H, 7·2, 7·1. $C_{31}H_{32}ON_2$ requires C, 83·0; H, 7·1%). The *ketone* dissolves readily in chloroform or carbon disulphide, is fairly easily soluble in ether or petroleum, less soluble in benzene or acetone, and very sparingly soluble in

ethyl or methyl alcohol. Its behaviour towards ketonic reagents was not examined, as the less complex dibenzhydryl ketone was known to be inert towards hydroxylamine, phenylhydrazine, and semicarbazide (Vorländer and Rack, *Ber.*, 1923, **56**, 1126).

The oil remaining after the ketone has been removed is fractionally distilled; the greenish-brown oil that passes over at 175°/2—3 mm. solidifies when cooled and scratched. By crystallising it from petroleum, *p*-dimethylaminodiphenylmethane (Limpricht, *Annalen*, 1899, **307**, 310) is obtained in thin leaflets, m. p. 31° (Found: C, 85·6; H, 8·0. Calc., C, 85·3; H, 8·0%).

Ethyl Phenyl-4-pyridylpyruvate (IX).—To a solution of potassium ethoxide (1 g. potassium) in 4 g. of alcohol are added in turn ether (20—30 c.c.), ethyl oxalate (3·8 g.), and 4-benzylpyridine (4·3 g.; 1 mol.). After 12 hours, the yellow potassium salt that has been deposited is decomposed by a slight excess of glacial acetic acid, ice-water added, and the ester together with the uncondensed material extracted with ether. From the washed and dried extract a solid is obtained which separates from alcohol in glistening, yellow crystals, melting at 123—124° to a yellowish-green liquid (yield about 33%) (Found: C, 71·3; H, 5·7; N, 5·4. $C_{16}H_{15}O_3N$ requires C, 71·4; H, 5·6; N, 5·2%). The *ester* is fairly easily soluble in benzene, chloroform, or acetone, less soluble in ethyl or methyl alcohol, sparingly soluble in ether, and insoluble in light petroleum.

The ester is left over-night in a cold dilute alcoholic solution of sodium hydroxide, water is then added, and the unchanged material removed with ether. The alkaline solution is acidified with acetic acid and shaken with chloroform. The chloroform in the extract is evaporated in a current of air, and the residue is freed from acetic acid by soda-lime in a desiccator. *Phenyl-4-pyridylpyruvic acid* is thus obtained as a yellow oil which solidifies when rubbed with benzene or crystallised from alcohol. It turns green at 100° and melts indefinitely at 110° (Found: C, 72·7; H, 5·2; N, 6·1. $C_{14}H_{11}O_3N$ requires C, 69·7; H, 4·6; N, 5·8%). The acid is very soluble in alcohol, acetic acid, or acetone, less soluble in benzene, and very sparingly soluble in light petroleum.

Phenylpyridylpyruvic acid oxime hydrochloride is obtained by mixing equivalent quantities of hydroxylamine hydrochloride and sodium phenylpyridylpyruvate in aqueous solution; crystals, m. p. 52—53°, of the *hydrochloride* are deposited after 12 hours (Found: C, 57·4; H, 4·3. $C_{14}H_{12}O_3N_2,HCl$ requires C, 57·4; H, 4·4%).

Sodium Phenyl-4-pyridylacetate.—On addition of the calculated quantity of hydrogen peroxide (30%) to an aqueous solution of

sodium phenylpyridylpyruvate, there is a rapid evolution of gas; the colour is completely discharged in about 1 hour. The solution of the sodium salt thus obtained, on being acidified, gives some 4-benzylpyridine, which is probably produced by decomposition of phenylpyridylacetic acid.

2-α-4-*Pyridylbenzyl*-3-*quinoxalone*, $C_6H_4<\begin{matrix}N=C\cdot CHPh\cdot C_5NH_4\\ NH\cdot CO\end{matrix}$.—Alcoholic solutions of equimolecular quantities of ethyl phenyl-4-pyridylpyruvate and *o*-phenylenediamine are heated together on a water-bath for 2 hours; the solid that separates is washed, and crystallised from hot pyridine; m. p. 294—295° (Found: C, 76·7; H, 4·8; N, 13·0. $C_{20}H_{15}ON_3$ requires C, 76·7; H, 4·8; N, 13·4%).

This work was carried out under the supervision of Dr. W. H. Mills, F.R.S., and the author is indebted to Prof. Sir William Pope for providing facilities in the laboratory.

University Chemical Laboratory,
Cambridge. [*Received, July 30th*, 1925.]

NOTES.

Selenium as a Chlorine Carrier. By Oswald Silberrad and Charles A. Silberrad.

The observations (Silberrad, C. A. Silberrad, and Parke, this vol., p. 1724) that selenium acted as a catalyst towards sulphuryl chloride in a perfectly normal manner, *i.e.*, midway between tellurium and sulphur, and that the catalysts examined appeared to behave as chlorine carriers rather than as dissociation catalysts made it of interest to reinvestigate Willgerodt's work (*J. pr. Chem.*, 1885, **31**, 539; 1888, **34**, 264) on direct chlorination, which led him to the conclusion that selenium does not act, in that case, as a chlorine carrier at all.

To this end dual experiments were conducted. Chlorine (1 mol.) was passed into boiling toluene (1) without and (2) with the addition of selenium chloride; each experiment was repeated (*a*) in total darkness and (*b*) in an apparatus so arranged that the vapour was exposed to light; the quantities of chlorotoluene and benzyl chloride produced were determined as recently described (*loc. cit.*). The results were as follows:

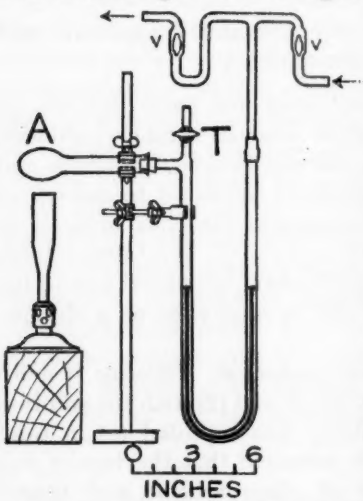
Conditions of expt.	$d_4^{16°}$.	Composition of product %. Chlorine.	Toluene.	Chlorotoluene.	Benzyl chloride.	Ratio Chlorotoluene/benzyl chloride.
		(*a*) In total darkness.				
No catalyst	0·961	12·4	55·8	2·7	41·5	0·065
With selenium (1·0 g. of $SeCl_4$)*	0·983	15·8	43·4	33·7	22·9	1·472
		(*b*) Vapour exposed to light.				
No catalyst	0·988	16·2	42·3	10·6	47·1	0·225
With selenium (0·3 g. of $SeCl_4$)*	1·004	18·3	34·6	29·5	35·9	0·82

* The selenium chloride was prepared by passing dry chlorine over the element, with which, contrary to the literature (Sacc, *Ann. Chim. Phys.*, 1848, **23**, 124), both varieties react at the ordinary temperature, passing through the mono- to the tetra-chloride.

From these results it is evident that, contrary to the literature, selenium does act as a carrier in direct chlorination; its presence not only raises the ratio of nuclear to side-chain substitution, but also, to a lesser extent, increases the amount of chlorine which enters into combination in a given time.—THE SILBERRAD RESEARCH LABORATORIES, BUCKHURST HILL, ESSEX. [*Received, August 11th*, 1925.]

A Simple Form of Gas Circulating Apparatus. By A. R. PEARSON and J. S. G. THOMAS.

FOR circulating a volume of gas through a closed system, apparatus depending on the force-pump principle has been described by Bone and Sarjant (*Proc. Roy. Soc.*, 1919, **96**, *A*, 126) and by Davis, Place, and Edeburn (*Fuel*, 1925, **4**, 290); in each case the piston is mercury contained in a U-tube.



A prime mover for the mercury–U-tube type of circulating pump can be made very simply from ordinary laboratory apparatus, utilising the principle of the hot-air engine (see Griffiths, "The Thermal Measurement of Energy," 1901, p. 50). The complete apparatus is shown in the figure. The bulb A is heated by a burner, and when a pressure difference of two or three inches is indicated by the U-tube the mercury is set in oscillation by quickly opening

and closing the tap, T, in such a way that the pressure in the hot bulb is suddenly reduced as nearly as possible to equality with that on the other side of the U-tube. The mercury will then continue to oscillate as long as heat is supplied to the bulb, and by the operation of the glass valves, V, or other suitable valves, gas can be forced through the system in the direction of the arrows. To ensure regularity of operation, suitable dimensions must be chosen for the mercury column and the hot bulb. With the dimensions shown, the apparatus drives about 2 cubic feet of gas per hour against a total back pressure of about 3 inches of water.—South Metropolitan Gas Co., London, S.E. 15. [*Received, July 15th*, 1925.]

The Action of Metals on Dipentene Dihydrohalide. Preparation of a Synthetic Diterpene. By Kenneth Charles Roberts.

Alcoholic solutions of *cis*- and *trans*-dipentene dihydrobromide and of *trans*-dipentene dihydrochloride were each shaken at room temperature with molecular silver until reaction was complete, this being indicated when no precipitate was formed on dilution of a portion of the reaction mixture with water. The action of finely-divided copper was tried in the same way. (The action of sodium was investigated by Montgolfier, *Ann. Chim. Phys.*, 1880, **19**, 155). In no case was metal halide formed. There was therefore no condensation, but simply loss of halogen acid and production of dipentene. This polymerised to a diterpene, which was isolated as a colourless, highly viscous liquid with a faint terpene-like odour, b. p. 173—183°/13 mm., $n_D^{20°}$ 1·5170, $d^{20°}$ 0·9361 (Found: C, 88·4; H, 12·0; *M*, 273, 266; iodine value, 103. $C_{20}H_{32}$ requires C, 88·2; H, 11·8%; *M*, 272; iodine value, for one double linking, 94). β-Camphorene has b. p. 170—180°/10 mm., n_D 1·5180, and $d^{20°}$ 0·9300 (Semmler and Rosenberg, *Ber.*, 1913, **46**, 768).—University of Otago, New Zealand. [*Received, August 11th*, 1925.]